Corrective Action Plan

Naval Exchange Service Station

Naval Air Station Memphis

Millington, Tennessee

Prepared for:

DEPARTMENT OF THE NAVY

SOUTHERN DIVISION

NAVAL FACILITIES ENGINEERING COMMAND

CHARLESTON, SOUTH CAROLINA

Prepared by:

U.S. Geological Survey

Water Resources Division

720 Gracern Road, Suite 129

Columbia, South Carolina 29210

November 1993

Corrective Action Plan

Naval Exchange Service Station

Naval Air Station Memphis

Millington, Tennessee

Prepared for:

DEPARTMENT OF THE NAVY

SOUTHERN DIVISION

NAVAL FACILITIES ENGINEERING COMMAND

CHARLESTON, SOUTH CAROLINA

Prepared by:

U.S. Geological Survey
Water Resources Division
720 Gracern Road, Suite 129
Columbia, South Carolina 29210

November 1993

· 2001

Contents

1.0 INTRODUCTION	N
1.1 Summary	y of Environmental Assessment Report Findings8
1.1.1	History of Contamination8
1.1.2	Site Geology9
1.1.3	Site Hydrogeology10
1.1.4	Cleanup Levels for Soil and Ground Water12
1.1.5	Nature and Extent of Contamination13
	Soils13
	Ground Water13
2.0 CORRECTIVE	ACTION PLAN14
2.1 Correct	tive Actions Considered14
2.1.1	Soil Corrective Action14
	Vacuum Extraction15
	Costs15
	Enhanced Bioremediation15
	Costs17
	Non-Enhanced Bioremediation18
	Costs19
2.1.2	Ground Water Corrective Action20
	Ground Water Recovery with Activated Carbon
·	Absorption21
	Costs22
	Enhanced Bioremediation22
	Costs23
	Non-Enhanced Bioremediation24
	Costs25

2.2	Corrective Actions Chosen26
	2.2.1 Soil Corrective Action26
	2.2.2 Ground Water Corrective Action26
2.3	Corrective Action Plan Costs28
2.4	Proposed Implementation Schedule29
2.5	Signature Page30
Sele	ected References31

Figures

Figures	1.1-1.5	Maps	showing:
		1.1	Location f study area8a
-		1 2	Location of monitoring wells at the Newsl Each
		1.2	Location of monitoring wells at the Naval Exchange
			Service Station9a
	u.	1.3	Areas where concentrations of benzene in ground water at
			the Naval Exchange Service Station site exceeded 2,000
			micrograms per liter 1987-929b
		1.4	Water levels in the surficial aquifer,
	·		December 8, 199210a
		1.5	Areas where Total Petroleum Hydrocarbon concentrations in
			soils exceeded cleanup levels of 500 milligrams per
			kilogram at depths of 6-8 feet below
			land surface 1990

<u>Tables</u>

Table 2.	.1 Co	st Schedule	for	Non-Enhanced	Bioremediation.	<i>.</i> 29
----------	-------	-------------	-----	--------------	-----------------	-------------

Appendixes

- Appendix A.--Evaluation of Enhanced and Non-Enhanced Biodegradation as

 Options for Remediating Petroleum Hydrocarbon Contamination, Naval

 Exchange, Naval Air Station Memphis.
- Appendix B.--Evaluation of Vacuum Extraction as a Remediation Option
- Appendix C.--Harding Lawson Associates evaluation of Biodegradation as a remediation option.
- Appendix D.--Laboratory data sheets for ground water samples taken December 8-12, 1992.

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	Ву	To obtain
foot (ft)	0.3048	meter
foot per day (ft/d)	0.3048	meter per day
foot per foot (ft/ft)	1.00	meter per meter
gallon per minute (gal/min)	0.06309	liter per second
milligram per kilogram	1.00	parts per million
per day [(mg/kg)]		per day
centimeter per second (cm/s)	0.03281	foot per second
gram (g)	0.03527	ounce

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:

 $^{\circ}F = 1.8 \times ^{\circ}C + 32$

Sea level: In this report "sea level" refers to the National Geodetic

Vertical Datum of 1929 - a geodetic datum derived from a general adjustment of
the first-order level nets of both the United States and Canada, formerly
called Sea Level Datum of 1929.

Abbreviations

microgram per liter - μg/L

micromole per liter - μmol/L

millimole per liter - mmol)

microcuries per milliliter - μCi/mL

1.0 Introduction

The following is a corrective action plan (CAP) for existing petroleum hydrocarbon contamination at the Naval Exchange Service Station, Naval Air Station Memphis (NAS Memphis), at Millington, Tennessee (fig. 1.1). The CAP was prepared following completion of a Final Remedial Action Plan (Harding Lawson Associates, 1988), a Vacuum Extraction Pilot Study and Remedial Investigation Report by ERC Environmental and Energy Services Company (ERCE), 1990, and an Evaluation of Enhanced and Non-Enhanced Biodegradation as a Remedial Option by the U.S. Geological Survey (Appendix A).

In the following sections, the CAP summarizes the findings of these studies regarding the evaluated corrective action options, and detailed specifications, and cost estimates for the chosen corrective action.

1.1 Summary of Environmental Assessment Report (EAR) Findings

Site characterization and assessment of the site at the Naval Exchange Service Station have been ongoing since 1987. The main findings of these studies (Harding Lawson and Associates, 1987; Harding Lawson and Associates, 1988; ERC Evironmental and Energy Sevices Company, 1989; ERC Environmental Services and Energy Company, 1990) are summarized below.

1.1.1 History of Contamination

A gasoline leak was discovered at the Naval Exchange Service Station in February 1986 during a routine inventory of fuel. The loss of fuel, estimated to be 5,000 gallons, was immediately reported to the Tennessee Department of Health and Environment. It was discovered that a pipe joint on a buried regular unleaded gasoline line was leaking. The pipe joint was replaced and subsequent inventories indicated no further releases of gasoline.

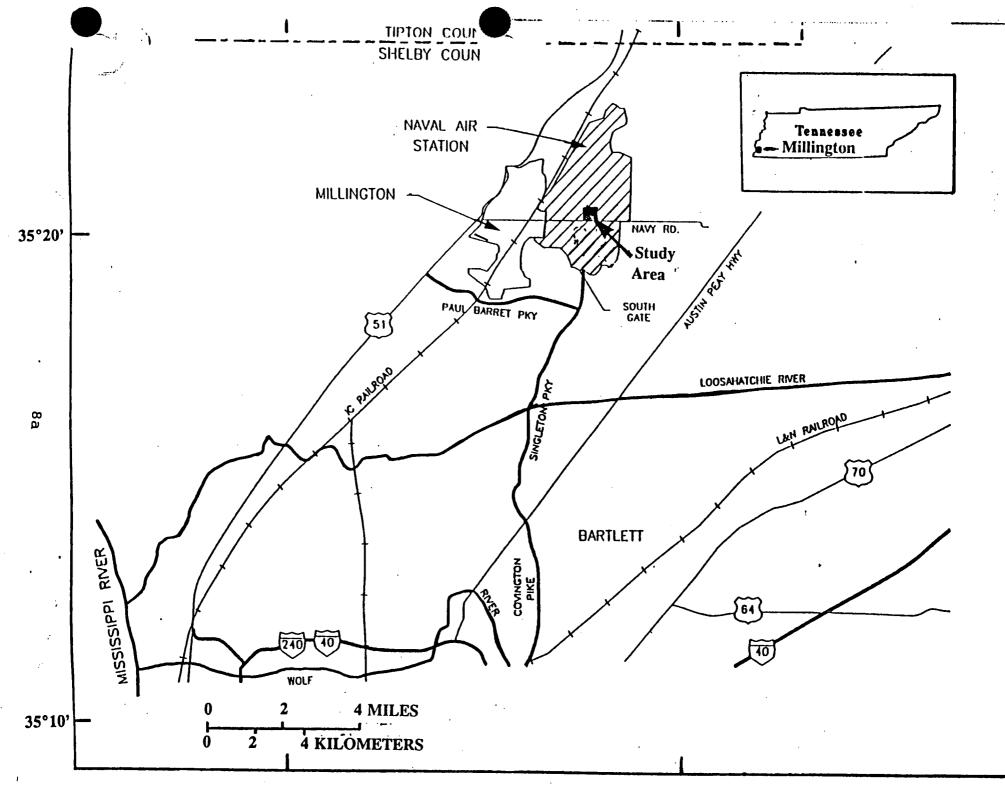
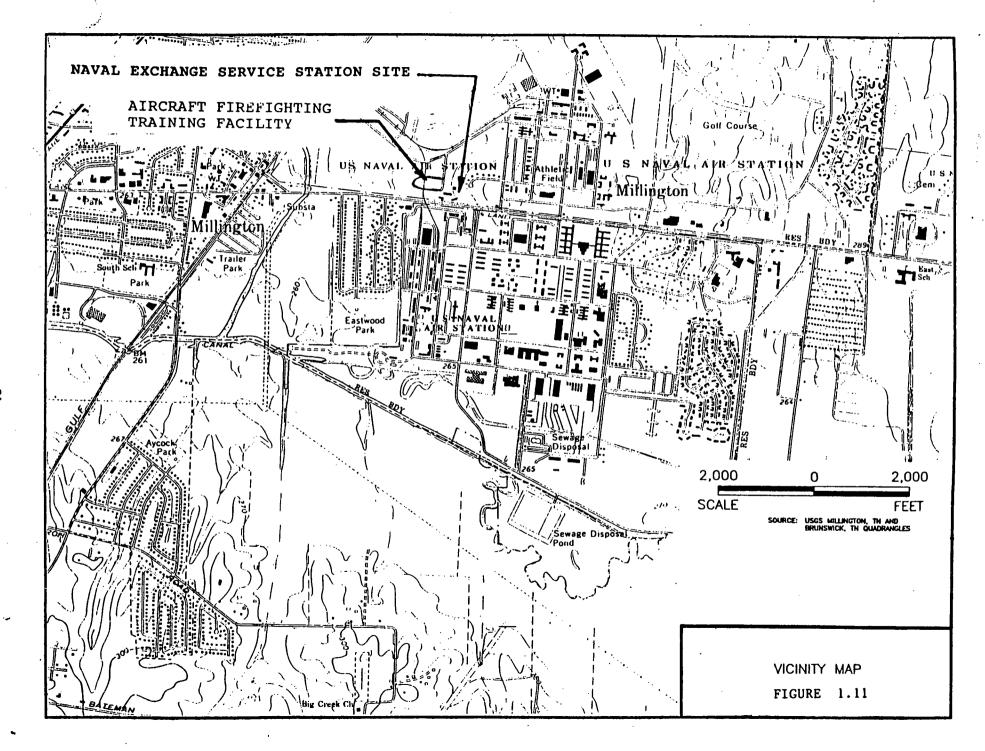


Figure 1.1 -- I onation of study area



Subsequent studies at the site (ERC Environmental Services and Energy Company, 1990) indicated that as many as three leaks occurred at different parts of the facility, and that fuel losses totaled as much as 5,400 gallons. A m re precise estimate of the amount of fuel spilled at the site cannot be made from existing records. The distribution of contaminated ground water at the site indicates three zones of substantial hydrocarbon contamination (ERCE, 1990). One zone is centered near the existing pump islands and is related to the original leaking pipe joint. Another contaminated zone is in the area of the underground storage tanks (UST), and the third contaminated zone is near the oil-water separator (fig. 1.2). Two other areas of hydrocarbon-contaminated sediment, one south of the Automotive Exchange Building and the other south of Building 341, were identified from soil borings (ERCE, 1990). The area of the pump islands exhibits the highest concentrations of dissolved hydrocarb n contamination, the UST somewhat lower concentrations, and the oil-water separator the lowest concentrations.

The movement of benzene, toluene, ethylbenzene, and xylene (BTEX) contaminants was monitored at the site from 1986 through 1992. The monitoring data indicate that contaminated ground water has not moved from the immediate vicinity of the spills (fig. 1.3). Furthermore, concentrations of benzene in water from some of the wells declined during this period. Benzene concentrations in water from well MEM-757-B2, for example, decreased from $6.800~\mu\text{g/L}$ to $2.810~\mu\text{g/L}$ during this period.

1.2 Site Geology

The Naval Exchange site is underlain by fine-grained alluvial sediments. The sediments consist primarily of reworked glacial loess with some lenses of sand-sized material. The lithology of these sediments is illustrated by the

lithologic logs of boring near well MEM-757-17 (fig. 2a, Appendix A) and MEM-757-16 (fig. 2b, Appendix A). The deepest sediments penetrated by the boring were brown clays and silts, which appear to be undisturbed glacial loess. The loess is overlain by a thin lens of fine sand, which probably records inchannel sedimentation in a small stream. The lithology at this site indicates that most of the sediments were deposited in flood plain and overbank environments. The decomposed plant material observed in the layers of silty clay are consistent with this interpretation.

1.1.3 Site Hydrogeology

The fine-grained sediments at the study site are characterized by relatively low hydraulic conductivities. Extensive hydrologic testing, which included aquifer tests conducted by ERCE (1990), indicated hydraulic conductivities on the order of 1 ft/d.

Water levels in the surficaial aquifer at the site, measured on December 8, 1992, (fig. 1.4) indicate that ground water moves onto the site from the east, and moves either toward the drainage ditch on the south side of Old Navy Road, or toward a marshy area to the north of the site. Because the site is almost entirely covered by macadam blacktop, vertical recharge to the surficial aquifer is limited to the grassy area on the eastern border of the site.

The measured hydraulic conductivities and the water-level data allow rates of ground-water flow to be estimated using Darcy's Equation:

$$v = (K dh/dx)/P$$
 , (1)

where:

v is the average velocity of ground water in feet per day,

K is the average hydraulic conductivity in feet per day),

dh/dx is the hydraulic gradient (dimensionless), and

P is sediment porosity (dimensionless).

In the vicinity of the underground storage tanks (fig. 1.4), water levels decreased from about 269 feet to 265 feet above sea level over a lateral distance of about 200 ft. This decrease gives a dimensionless hydraulic gradient of 0.02. Given a hydraulic conductivity of 1 ft/d (ERCE, 1990) and assuming a porosity of 0.3, which is typical of silty materials, the average ground-water flow velocity is estimated to be 0.067 ft/day. At this velocity, a non-reactive solute would have been transported about 170 feet in the 7 years since the spills were discovered. However, Well MEM-757-15, which is about 55 feet downgradient of the underground storage tank zone (Well B2), does not show measurable levels of contamination (Table 1, Appendix A). This, in turn, indicates that the hydrocarbon contaminants are reactive and are being retarded relative to ground-water flow.

1.1.4 Cleanup Levels for Soil and Ground Water

A STATE OF THE STA

Under Tennessee regulations, cleanup levels for soil and ground water are established on the basis of sediment permeability and the classification of ground water as either drinking water or non-drinking water. An Environmental Assessment Report (EAR) prepared for the Aircraft Firefighting Training Facility at Memphis NAS, which is immediately adjacent to the Naval Exchange did not indicate any use of shallow ground water within one mile of the site (EnSafe/Allen & Hoshall, 1992). Thus, ground water at the site is classified as non-drinking water. The hydraulic conductivity at the Naval Exchange has been investigated by several contractors (Harding Lawson Associates, 1987; ERCE, 1990) and has been found to be in the range of from 0.1 to 1.0 ft/d (10⁻⁴ to 10⁻⁵ cm/sec). For sediments that have a hydraulic conductivity in the range noted above, and water classified in the non-drinking category, applicable cleanup levels for soil are 250 mg/kg for BTEX, and 500 mg/kg for total petroleum hydrocarbons (TPH). Similarly, cleanup levels for ground water are 0.07 mg/L for benzene and 1.0 mg/L for TPH.

1.1.5 Nature and Extent of Contamination

Soils

TPH concentrations in soils that exceed cleanup levels are present south f the pump islands (1,900 mg/kg TPH), south of Building 341 (15,000 mg/kg TPH) and south of the Automotive Exchange Building (1,100 mg/kg TPH) (ERCE, 1990). Figure 1.5 shows zones where TPH concentrations in soils exceeded cleanup levels.

Ground Water

The concentration of contaminants in ground water exceeded cleanup levels in the area immediately south of the pump islands, and in the vicinity of the UST (fig. 1.3). Near the UST, benzene concentrations in ground water ranged from 0.125 to 2.8 mg/L, and TPH concentrations in ground water ranged from 10 to 35 mg/L. South of the pump islands, benzene concentrations ranged from 0.165 to 14 mg/L and TPH concentrations ranged from 2 to 35 mg/L.

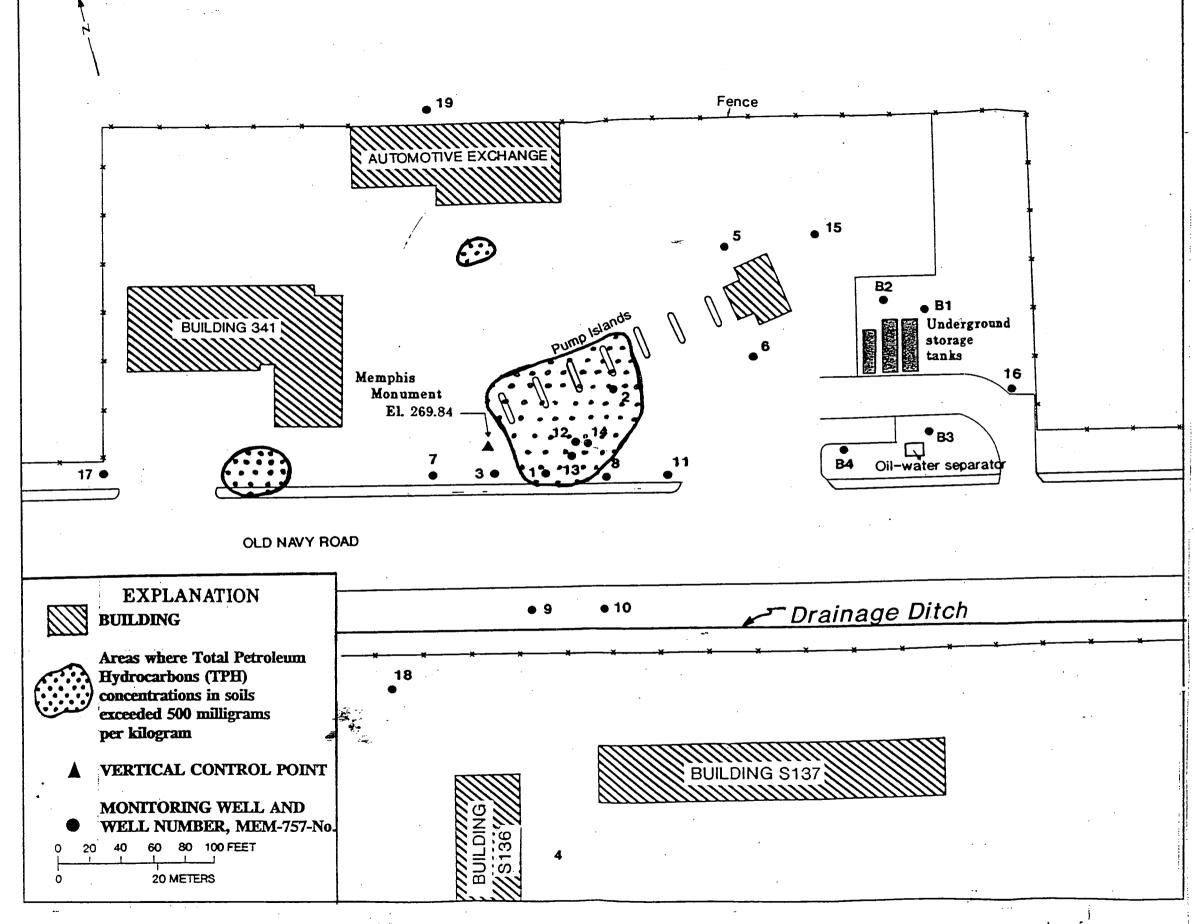


Figure 1.5.— Areas where Total Petroleum Hydrocarbons (TPH) concentrations in soils exceeded cleanup levels of 500 milligrams per kilogram at depths of 6-8 feet below land surface, 1990.

2.0 CORRECTIVE ACTION PLAN

This Corrective Action Plan (CAP) will provide general information concerning the corrective actions that were evaluated and the specifications and costs for the corrective action options that were chosen. This section of the CAP was completed upon review of the contaminant plumes delineated in previous studies and their current status as determined during evaluation of biodegradation as a remediation option at this site (Appendix A).

2.1 CORRECTIVE ACTIONS CONSIDERED

2.1.1 Soil Corrective Action

At the site, contaminant levels in surface soils and sediments from 2 to 4 feet below land surface do not exceed cleanup levels (ERCE, 1990). The absence of near-surface contamination reflects the fact that contamination was introduced below grade (such as the leaking pipe joint) rather than spilled at land surface. However, just south of the pump island, sediments at depths of 6 to 8 feet below grade had a maximum TPH concentration of 1,600 mg/kg TPH and sediments at depths of 8 to 10 feet had a maximum TPH concentration of 1,900 mg/kg. Sediments at depths of 10 to 12 feet below grade at this location had TPH concentrations of 900 mg/kg or less.

Three technologically feasible and reliable corrective action options were considered for the remediation of petroleum-contaminated sediments and soils to the applicable cleanup levels. These options were:

- (1) Vacuum Extraction
- (2) Enhanced Bioremediation
- (3) Non-Enhanced Bioremediation

Vacuum Extraction - Vacuum extraction has been widely employed to remediate hydrocarbon-contaminated sediments in a variety of geologic settings. The potential for applying this technology at the Naval Exchange Service Stati n site was evaluated by ERCE (1990). The ERCE study (Appendix B) concluded that, because of the low permeability of the sediments and because much of the contaminated sediment was below the water table, a large number of extraction wells (approximately 1,100) would be needed to lower the water table sufficiently to effect remediation.

Costs - The cost of this option was not determined by ERCE. But it was concluded that, based on the number of extraction wells needed and associated piping for water and air, the costs would be prohibitive.

Enhanced Bioremediation - Enhanced bioremediation is a technology that is widely applied to petroleum hydrocarbon contamination of soils. Its major advantage over vacuum extraction is that it can lead to the removal of n n-volatile as well as volatile compounds.

The feasibility of using nutrient-enhanced bioremediation was assessed by the U.S. Geological Survey (Appendix A) and Harding Lawson Associates (1988; Appendix C). The Harding Lawson study reported that benzene, toluene, and xylene (BTX) were removed more rapidly from soil-water slurries under enhanced (addition of ammonium nitrate and potassium phosphate) conditions than under non-enhanced conditions (Plate 14, Appendix C). The study also indicated that total light hydrocarbons associated with the soil (Plate 15, Appendix C) were removed under both enhanced and non-enhanced conditions. Total BTX loss (Plate 17, Appendix C) and loss of light hydrocarbons from soils were slightly higher under enhanced than under non-enhanced conditions. Growth of

microorganisms in laboratory incubations (Plate 19, Appendix C) was slightly higher under enhanced conditions relative to non-enhanced conditions.

A U.S. Geological Survey study (Appendix A) used different methods than Harding Lawson Associates (1988) but arrived at similar conclusions. When non-contaminated sediments were incubated with ¹⁴C-labeled toluene (fig. 7, Appendix A), mineralization of the toluene to ¹⁴CO₂ was more rapid under nutrient-enhanced conditions than under non-enhanced conditions. However, in sediments with significant contamination (fig. 8, Appendix A), addition of nutrients did not increase rates of toluene degradation. These results indicate that for heavily-contaminated soils, nutrient enhancement may increase rates of hydrocarbon loss but the increase is likely to be modest.

The low permeability of sediments underlying the Naval Exchange Servic Station places constraints on enhanced bioremediation. The most widely used design for enhanced bioremediation is to inject nutrients by means of injection wells (Hutchins and others, 1991). This procedure works well in high-permeability sediments but is less efficient in low-permeability sediments such as those underlying the Naval Exchange Service Station Site. Recent studies of bioremediation have concluded that aquifer sediments with permeabilities less than 10⁻⁴ cm/sec are unsuitable for enhanced bioremediation (National Research Council, 1993). Because sediment permeability at the Naval Exchange Service Station site is 10⁻⁴ cm/sec or less, the efficiency of nutrient delivery to contaminated sediments will be marginal.

Costs - In addition to the costs of constructi n and maintenance of an enhanced bioremediation system, c sts would be incurred in m nitoring the effectiveness of the system. It is proposed to monitor BTEX and gasoline-range organics (GRO) TPH concentrations in sediments at four locations and at 5 depths at each location. The locations to be monitored are the four major areas of soil contamination near well MEM-757-B2 (near the UST), near wells MEM-757-1 and MEM-757-2 (near the pump island), near boring location A-9 (ERCE, 1990, south of the Automotive Exchange Building), and near boring location A-19 (ERCE, 1990; south of Building 341). Costs associated with a single sampling run for BTEX and TPH (GRO) are as follows.

BTEX and TPH analyses, 20 samples each	\$6,000
Sampling Crew, 3 days	\$2,000
Split-spoon coring rig, 3 days	\$5,500

Total \$13,500

The monitoring schedule suggested for the CAP is to monitor the site for soil BTEX and TPH (GRO) on a yearly basis for five years, with an evaluation of the effectiveness of the enhanced bioremediation strategy at the end of this period.

Non-Enhanced Bioremediation - Non-enhanced bioremediation is the process by which naturally occurring populations of microorganisms degrade contaminants in place. The feasibility of non-enhanced bioremediation for soils was addressed by Harding Lawson Associates (1988; Appendix C). Their study indicated that indigenous microorganisms capable of degrading petroleum hydrocarbons are present at the site and that degradation of hydrocarbons in sediments occurs at measurable rates. Determining rates of biodegradation in place, as opposed to determining such rates in the laboratory is problematical. The Harding Lawson laboratory data suggest degradation rates from 0.7 to 9.5 mg/kg/d for light petroleum hydrocarbons (plate 18, Appendix C). Such rates would reduce hydrocarbon contamination in sediments below cleanup levels within 10 years. The U.S. Geological Survey laboratory evaluation of BTEX degradation (Appendix A), which documented rates at which $^{14}\text{C-labeled}$ toluene was degraded to $^{14}\text{CO}_2$, indicated toluene degradation rates of 2.5 mg/kg/d. These rates are similar to those indicated by the Harding Lawson Associates study. However, because petroleum hydrocarbon concentrations in sediments at the site have not been monitored with time. it is not possible to compare the laboratory-measured rates to rates occurring in place. It is commonly observed, however, that degradation in place proceeds slower that in laboratory incubations (Hutchins and others, 1991).

Costs - The principal costs associated with n n-enhanced bioremediation are costs for continued monitoring to verify that concentrations of soil contaminants are being reduced. It is suggested that BTEX and gasoline-range organics (GRO) TPH concentrations in sediments be monitored at four locations and at 5 depths at each location. The locations to be monitored are the four major areas of soil contamination near well MEM-757-B2 (near the UST), wells MEM-757-1 and MEM-757-2 (near the pump island), near boring location A-9 (ERCE, 1990, south of the Automotive Exchange Building), and near boring location A-19 (ERCE, 1990; south of Building 341). Costs associated with a single sampling event for BTEX and TPH (GRO) are as follows.

BTEX and TPH analyses, 20 samples each	\$6,000
Sampling Crew, 3 days	\$2,000
Split-spoon coring rig, 3 days	\$5,500

Total \$13,500

For the CAP, it is suggested that soil BTEX and TPH (GRO) be monitored at the site on a yearly basis for 5 years, with an evaluation of the effectiveness of the non-enhanced bioremediation strategy at the end of this time.

2.1.2 Ground-Water Corrective Action

Concentrations of TPH in ground water exceed cleanup levels in the area south of the pump island and near the UST's. More detailed descriptions of ground-water contamination are presented in reports by Harding Lawson Associates (1987), ERCE (1990), and in Appendix A.

The shallow ground water in the vicinity of the Naval Exchange Service Station Site is classified as non-drinking water on the basis of water-use and water-quality data (Ensafe/Allen & Hoshall, 1992). For sediments with permeabilities from 10^{-4} to 10^{-6} cm/sec, the applicable cleanup levels are 0.07 mg/L for benzene and 1.0 mg/L for TPH (GRO).

Three technologically feasible corrective action options were considered to remediate petroleum-contaminated ground water to the applicable cleanup levels. These options were:

- (1) Ground-Water Recovery with Activated Carbon Adsorption
- (2) Enhanced Bioremediation
- (3) Non-Enhanced Bioremediation

Ground Water Recovery with Activated Carbon Adsorption - For this option, ground water would be removed by the use f recovery wells, tr ated with carbon adsorption, and discharged to the Millington Publicly Owned Treatment Works (POTW). The process of retrieving the ground water would serve to hydraulically contain the contamination. Also, because of the large number of available wells, new wells would not need to be drilled. On the basis of the site aquifer characteristics, it is estimated that the existing wells, pumped at a rate of approximately 0.5 gal/min, could be used to collect contaminated ground water.

Carbon adsorption can be used to treat/remove liquid and vapor-phase volatile organic compounds from contaminated water. Contaminated water flows through a packed column of granular activated carbon where the organic compounds are removed by physical and chemical adsorption. Physical adsorption works by forming molecular condensation in the capillaries of the solid, whereas chemical adsorption requires formation of a monomolecular layer of the contaminant on the surface of the activated carbon. Carbon adsorption may be applied to liquid or vapor-phase organic materials.

Carbon adsorption treats contaminated liquid and vapor-phase volatile organics. The advantages of carbon adsorption are that the technology is readily available and implementable, and the capital cost is comparable to other organic removal systems. The disadvantages of carbon adsorption are the disposal of spent activated carbon (which may be classified as a hazardous waste), plugging of the carbon filters by precipitating iron and by suspended particles, and rapid depletion of the filter capacity by high organic carbon concentrations. Another disadvantage is that BTEX immobilized in aquifer sediments will continue to be solubilized as the pump and treat process is

ongoing. Because of the high sorptive capacity of the sediments underlying the Naval Exchange (Appendix A), it is anticipated that the pump and treat process would need to continue for greater than 10 years to remove most or all of the contaminants.

Costs - Capital costs for constructing and operating a carbon adsorption treatment system were estimated based on design criteria listed by EnSafe/Allen & Hoshall (1992). The estimated cost for construction is \$200,000, icluding the cost of two carbon adsorbers, equipment freight, replacement carbon, ten pumps, piping and electrical, engineering labor, macadam removal during piping installation, and macadam replacement. Estimated operation and maintenance cost for carbon adsorption will be approximately \$100,000 per year, based on expected rates of carbon replacement, electrical costs, and maintenance costs.

Enhanced Bioremediation - Nutrient-enhanced bioremediation is a process by which naturally occurring microbial processes in an aquifer are stimulated to facilitate degradation of pollutants. This is most commonly accomplished by addition of nutrients such as nitrogen and phosphorus that are not naturally abundant and which commonly limit rates of degradation. Harding Lawson Associates, 1988 (Appendix C, plate 14) reported that by adding nitrogen and phosphorous to samples of ground water, BTX biodegradation rates increased relative to samples to which no nutrients were added. Similarly, Harding Lawson Associates (1988) reported that this activity was due to microorganisms that were capable of growth on petroleum hydrocarbons.

More recent studies by the U.S. Geological Survey (Appendix A) have shown that BTX compounds are mineralized by indigenous microorganisms, but that

degradation rates under enhanced conditions were not substantially higher than under non-enhanced conditions. This indicates that micr bial activity at the Naval Exchange Service Station site is not limited by available nitrogen and phosphate and that addition of these compounds will not substantially increase rates of biodegradation.

Costs - An itemized capital cost for constructing an enhanced bioremediation system at the Naval Exchange Service Station site was not prepared. However, the cost for constructing a enhanced bioremediation system for a JP-4 jet fuel-contaminated aquifer in Hanahan, South Carolina, was approximately \$350,000 (Donald Matthews, Defence Logistics Agency, oral communication, 1993) and construction costs at the Naval Exchange Service Station site would probably be similar. The costs for operation and maintenace of the Hanahan site are approximately \$120,000 per year (Don Vroblesky, U.S. Geological Survey, oral communication, 1993), and costs for maintaining an enhanced bioremediation system at the Memphis NAS Naval Exchange Service Station site would also probably be similar.

Non-Enhanced Bioremediation - Data showing the efficiency of n n-enhanced bioremediation for containing and treating petroleum hydrocarbon-contaminated ground water has only recently been made available. During long-term monitoring of a crude oil spill in Bemidji, Minn., it has been shown that over a period of years, rates of non-enhanced biodegradation come into equilibrium with rates of contaminant transport (Baedecker et al., 1993). If rates of contaminant transport by ground-water flow are low compared to rates of non-enhanced biodegradation, hydrocarbon contamination is effectively contained near the source of contamination. Furthermore, degradation of petroleum hydrocarbons in ground water and in the sediment leads to an overall reduction in the mass of contaminants over time, and, under favorable conditions, reduces ground water hydrocarbon concentrations below cleanup levels.

The feasibility of using non-enhanced bioremediation at the Naval Exchange Service Station site was investigated by the U.S. Geological Survey (Appendix A). In this study, a combination of field and laboratory data was used to estimate degradation rates of toluene. This information was then combined with hydrologic data to estimate rates of ground-water flow at the site. By using an analytical equation that incorporated estimated rates of biodegradation and estimated rates of ground-water flow, it was estimated that concentrations of BTX in ground water would be restored below cleanup levels within 30 feet of contaminated soils, and that non-enhanced bioremediation likely will prevent contaminated water from reaching the nearest point of contact with humans. The results of this analysis are consistent with the observed distribution of BTX compounds at the site, and the observed lack of movement of the contamination plume over the previous 7 years. This evidence indicates that non-enhanced bioremediation is a technologically feasible

strategy for treating petroleum hydrocarbon-contaminated ground water at the site.

Costs - The principal costs associated with non-enhanced bioremediation are continued monitoring to verify that contaminated water is contained and that TPH and benzene concentrations are cleanup levels by the time the water is discharged to adjacent surface-water bodies. Costs associated with a single sampling event for BTEX and TPH (GRO) are as follows.

BTEX and TPH (GRO) analysis, 30 samples \$5,400
Sampling Crew, 3 days \$2,000
Total \$7,400

For the CAP, it is suggested that the site be monitored for BTEX and TPH on a quarterly basis for two years, for a total cost of \$29,600 per year. If the results of the quarterly sampling indicate that the plume of contaminated ground water is stationary, the sampling frequency could be reduced to once per year thereafter.

2.2 CORRECTIVE ACTIONS CHOSEN

2.2.1 Soil Corrective Action

The corrective action chosen by the Responsible Party to remediate contaminated soil is non-enhanced bioremediation. The ability of naturally occurring microorganisms to degrade hydrocarbons associated with soils at this site under non-enhanced conditions has been firmly established (Appendices A and C). Furthermore, the relatively modest increases of hydrocarbon biodegradation rates that can be achieved by nutrient addition do not justify the much higher cost of an enhanced biodegradation system. Because determination of the rate of non-enhanced biodegradation remains problematic, continued monitoring of the soils at this site on a yearly basis is an important component of the chosen corrective action.

2.2.2 Ground-Water Corrective Action

The corrective action chosen by the Responsible Party to remediate contaminated ground water is non-enhanced bioremediation. The ability of naturally occurring microorganisms to degrade hydrocarbons associated with ground water under non-enhanced conditions has been confirmed and documented (Appendix A, Appendix C) using both laboratory experiments and field monitoring data. The fact that contaminated ground water has not measurably moved in the 2-year period between January 1991 and December 1992 demonstrates that the plume is presently contained. The low rates of ground-water flow, and observed rates of biodegradation (Appendix A, p. 16-17) are the principal reasons for the observed containment of contaminated ground water. The aquifer is, in effect, functioning much like a bed of activated sludge in an aerobic digester. Contaminated ground water is continuously leached from the contaminated soils, and transported toward the discharge areas on either the north or south sides of the site. As this contaminated water is transported,

indigenous microorganisms metabolize the hydrocarbons. Applicati n of an analytical equation that incorporates c ntaminant transp rt by advective ground-water flow and biodegradation, indicates that water is brought t within cleanup levels over a 30-ft flowpath. Because flowpaths to the nearest possible points of discharge are greater than 100 ft in length, a sufficient buffer exists for non-enhanced bioremediation to bring contamination levels well within cleanup levels prior to discharge to any potential point of contact with humans.

An important component of the chosen corrective action is continued monitoring of ground water at this site to verify that contaminated ground water remains contained over time. Monitoring on a quarterly basis is proposed for the first 2 years, after which the monitoring could be reduced to annually if benzene and TPH are shown to remain immobilized.

2.3 CORRECTIVE ACTION PLAN COSTS

The principal costs associated with non-enhanced bioremediation are costs for monitoring soils and ground water. These costs are outlined in Table 2.1. The analytical cost is based on \$150 per sample for BTEX and \$150 per sample for TPH (GRO). Sampling sediments and ground water would take about 5 days. The sampling labor cost is based on two geologists and two drillers/technicians collecting the samples at \$35.00 per hour. The labor costs outlined in Table 2.1 include labor for sampling and for compiling status reports.

Table 2.1.--Cost Schedule for Non-Enhanced Bioremediation

ITEM		MONI	TORING YEAR		
	1*	2*	3**	4 ^{**}	5 ^{**}
Laboratory					· · · · · · · · · · · · · · · · · · ·
Analyses					
soil	\$7,200	\$7,300	\$7,400	\$7,500	\$7,60
water	\$21,600	\$21,600	\$6,000	\$6,300	\$6,60
Labor and Mate	erials		,	•	
soil	\$7,500	\$7,500	\$2,400	\$2,600	\$2,80
water	\$2,000	\$2,200	\$2,400	\$2,600	\$2,80
Sample					
Shipping	<u>\$300</u>	\$300	\$300	<u>\$300</u>	\$30
Subtotal	\$38,600	\$38,900	\$18,500°	\$19,300	\$20,10

^{*} quarterly sampling of ground water, annual sampling of sediments

2.4 PROPOSED IMPLEMENTATION SCHEDULE

It is proposed to begin monitoring the non-enhanced bioremediation system in April, 1994.

^{**}annual sampling of ground water and sediments.

2.5 SIGNATURE PAGE

This document has been approved by the Director of the U.S. Geological Survey. Such approval constitutes an affirmation that the technical interpretations in the document are supportable, that any stated conclusions are impartial and objective, and that the U.S. Geological Survey presents the interpretations as the best that could be made on the basis of the data available on the date of approval.

Francis H. Chapelle, Ph.D.

Hydrologist

November 17, 1993

Name

Title

Date

Signature

SELECTED REFERENCES

- Baedecker, M.J., I.M. Cozzarelli, D.I. Siegel, P.C. Bennett, and R.P.

 Eganhouse, 1993, Crude oil in a shallow sand and gravel aquifer: III.

 Biogeochemical Reactions and Mass Balance Modeling in Anoxic Ground

 Water, Applied Geochemistry, v. 8, 569-586.
- EnSafe/Allen & Hoshall, 1992, Environmental Assessment Report for Tank Systems

 1489 and 1508 Aircraft Firefighting Training Facility, Naval Air Station

 Memphis, Millington, Tennessee, 23 p.
- ERC Environmental and Energy Services Company, 1989, Final Supplemental

 Remedial Action Plan (RAP) Naval Exchange Service Station, NAS, Memphis,

 Tennessee, 16 p.
- ERC Environmental and Energy Services Company, 1990, Vacuum extraction pilot study and remedial investigation report, volume 1, 49 p.
- ERC Environmental and Energy Services Company, 1991, Quarterly Ground Water

 Sampling Report, Naval Exchange Service Station, Naval Air Station

 Memphis, Millington, Tennessee, 28 p.
- Harding Lawson Associates, 1987, Site Characterization Study, Naval Exchange Service Station, NAS Memphis, 29 p.
- Harding Lawson Associates, 1988, Final Remedial Action Plan (RAP), Naval Air Station Navy Exchange (NX) Service Station, Millington, Tennessee, 97 p.

- Hutchins, S.R., W.C. Downs, J.T. Wils n, G.B. Smith, D.A. Kovacs, D.D. Fine, R.H. Douglass, and D.J. Hendrix, 1991, Effect of nitrate addition on biorestoration of fuel-contaminated aquifer: Field demonstration. Ground Water 29(4):571-580.
- National Research Council, 1993, Bioremediation: How do we know when it works? National Academy Press, 147 p.

APPENDIX A

EVALUATION OF ENHANCED AND NON-ENHANCED BIODEGRADATION AS OPTIONS FOR REMEDIATING PETROLEUM HYDROCARBON CONTAMINATION, NAVAL EXCHANGE, NAVAL AIR STATION MEMPHIS, TENNESSEE

EVALUATION OF ENHANCED AND NON-ENHANCED BIODEGRADATION AS OPTIONS FOR REMEDIATING PETROLEUM HYDROCARBON CONTAMINATION, NAVAL EXCHANGE, NAVAL AIR STATION MEMPHIS, TENNESSEE

Francis H. Chapelle, Paul M. Bradley, and James E. Landmeyer

U.S. Geological Survey, WRD
720 Gracern Rd., Suite 129
Columbia, South Carolina 29210

November, 1993

prepared for:

COMMANDING OFFICER

SOUTHERN DIVISION, NAVAL FACILITIES ENGINEERING COMMAND
P.O. Box 100068

Charleston, South Carolina 29411-0068

EVALUATION OF ENHANCED AND NON-ENHANCED BIODEGRADATION AS OPTIONS FOR REMEDIATING PETROLEUM HYDROCARBON CONTAMINATION,

NAVAL EXCHANGE, NAVAL AIR STATION MEMPHIS, TENNESSEE

SUMMARY

Field and laboratory studies show that microorganisms indigenous to the ground-water system underlying the Naval Exchange Service Station degrade petroleum hydrocarbons at slow but measurable rates. (14 C) toluene was mineralized to 14 CO, at rates on the order of $10^{-4}~\mu\mathrm{mol}$ ${\tt L}^{-1}$ d⁻¹ and the process exhibited first-order degradation rate constants n the order of 0.03 day 1. Although these rates are low, they are significant in the hydrologic environment of this site. Because of low hydraulic conductivities (approximately 1 ft/d) and low hydraulic gradients (approximately 0.03 ft/ft), rates of ground-water flow are slow and range from 5 to 10 ft/year. Given these low rates of ground-water flow, rates f biodegradation effectively contain soluble BTEX hydrocarbons within a lateral distance of 10 to 30 feet from contaminated sediments. There is some evidence that addition of nitrogen and phosphate nutrients may increase rates of biodegradation, but the increase is small. The nearest potential point of human contact to contamination, under current site conditi ns, is a drainage ditch approximately 100 ft south of the the contaminated zone. Available evidence indicates that dissolved contaminants will be completely degraded before they reach this point. Non-enhanced biodegradation is thus an effective remediation alternative for addressing contaminated ground water at this site.

INTRODUCTION

In 1986, a gasoline leak was discovered at the Naval Exchange Service Station, Naval Air Station (NAS) Memphis, Tenn. The loss of fuel totaled approximately 5,000 gallons. The leak was reported to the Tennessee Department of Health and Environment, and an initial assessment of the contamination was made (Harding Lawson Associates, 1987). A follow-up study (Harding Lawson Associates, 1988) recommended that enhanced biodegradation was a feasible remediation option at the site. Subsequent to this, the feasibility of vacuum extraction as a remediation option was investigated (ERC, 1990). This study concluded that, due to low hydraulic conductivities observed at the site, vacuum extraction was not technologically feasible.

In the present report, the feasibility of enhanced and non-enhanced biodegradation of petroleum hydrocarbon contamination is evaluated. This evaluation consisted of field studies to document the present location and distribution of soluble hydrocarbons, principally benzene, toluene, ethylbenzene, and xylene (BTEX). Additionally, the presence of unstable intermediate products of hydrocarbon biodegradation, such as organic acids, was used to document in situ biotransformation of petroleum hydrocarbons. Finally, laboratory-derived rates of toluene (a model BTEX compound) degradation under enhanced and non-enhanced conditions were determin d.

The results indicate that hydrocarbons are being degraded at the site under in situ conditions. Rates of biodegradation at the site are low compared to rates reported at other sites. However, because of the unusually low rates of ground-water flow, biodegradation effectively confines the BTEX plume to within 10 to 30 ft of the contaminated sediments.

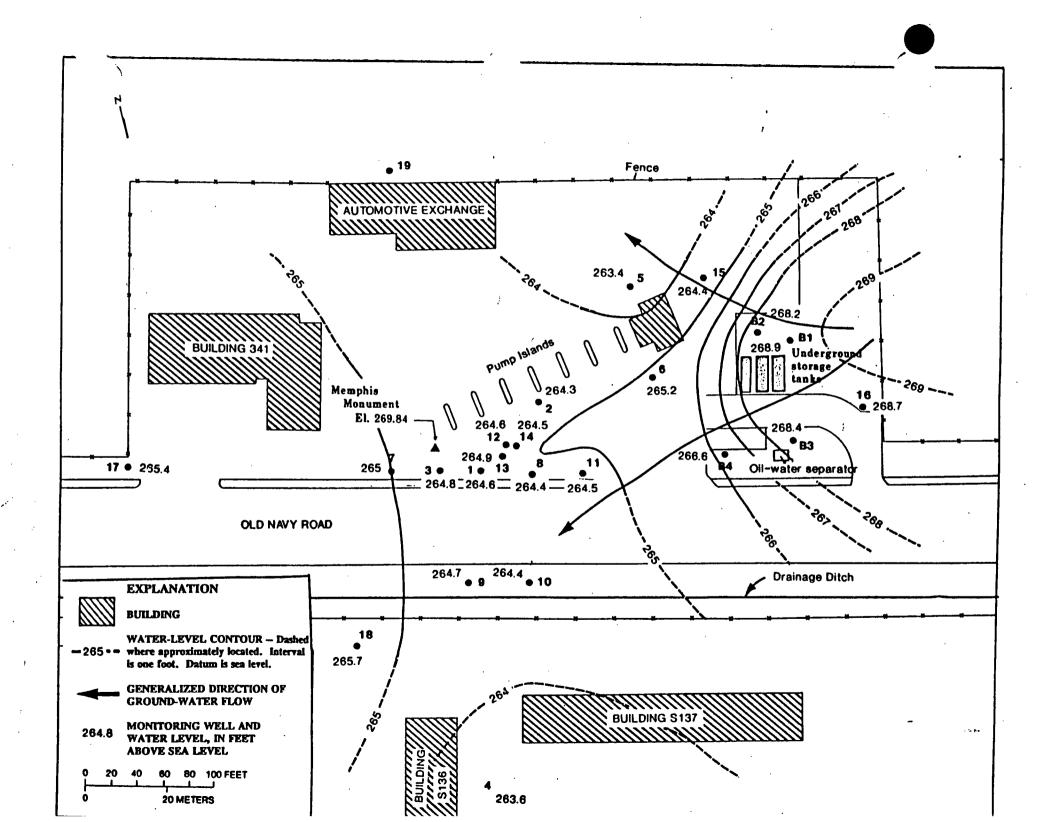
Based on laboratory experiments, the addition of nitrogen and phosphate nutrients to the ground-water system might increase rates of biodegradation, but the increase would likely be relatively small.

METHODS AND MATERIALS

Field Sampling

A site visit was made December 8-11, 1992, for the purpose of collecting water-chemistry data, water samples for BTEX analysis, and sediment samples for laboratory studies on BTEX biodegradation. Prior to ground-water sampling, water levels were recorded and then the wells purged (3 well-casing volumes). Measurements of water temperature, pH, and concentrations of dissolved oxygen, dissolved ferrous iron, and dissolved sulfide were made in the field using techniques described by Wood (1976) and Skougstad and others (1978). Samples were collected for BTEX and total petroleum hydrocarbons (TPH) for gasoline range organic (GRO) compounds and transported to the laboratory for analysis. Additional water samples were transported to the laboratory for analysis of short-chain aliphatic organic acids such as formate and acetate. Sediment samples were recovered from an uncontaminated site (MEM-757-17; Fig. 1) and a contaminated site (MEM-757-B1; Fig. 1) using a hand auger. Sediments were placed in pre-sterilized wide-mouth glass mason jars, chilled, and transported to the laboratory for analysis.

Laboratory Studies



Two independent methods were used to evaluate rates of BTEX degradati n in laboratory studies. The first method was similar to one described by Barker and others (1987). Triplicate vials were loaded with 50 grams (wet weight) of sediment, slurried with 150 mL of uncontaminated water from the site, and spiked with benzene, toluene, and xylene (BTX) to yield a final concentration of approximately 300 µmol/L for each compound. Duplicate vials were loaded in a similar fashion, amended with mercuric chloride to a final concentration of 5 mmol/L, and autoclaved for 30 minutes prior to addition of BTX to serve as microbiologically inactive controls. Vials were capped with Teflon¹-coated stoppers and crimped into place.

Concentrations of BTX were then monitored for 54 days using high pressure liquid chromatography (HPLC). In addition, concentrations of carbon dioxide (CO₂) were monitored in the headspace of the vials using gas chromatography with thermal conductivity detection.

The second method tracked production of ¹⁴CO₂ end-products from radiolabeled compounds as a measure of microbial activity. ¹⁴C labeled glucose was used to demonstrate the presence of microbial activity, and subsequent experiments used ¹⁴C labeled toluene to estimate rates of toluene degradation.

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Approximately 0.5 μ Ci of radiolabeled compound was added to 1.0 gm f sediments in each triplicate vial. Heat and mercury-killed controls were prepared as described above. At specified times, vials were acidified with phosphoric acid (H₃PO₄, 2.0 M), the evolved ¹⁴CO₂ collected in potassium hydroxide (KOH, 1.0 M) base traps, and ¹⁴C measured with liquid scintillation counting. Reported ¹⁴C values were corrected for activity in traps at time zero, and for background counts in the scintillation fluid (Ultima Gold, Packard Instrument Corporation). Reported activities are given as a percentage of added label.

RESULTS

Hydrologic Framework

The Naval Exchange site is located in the Gulf Coast Physiographic Province and underlain by fine-grained alluvial sediments of Pleistocene age. The sediments consist primarily of reworked glacial loess with some lenses of sand-sized material. The lithology of these sediments is illustrated by the lithologic log of a boring near well MEM-757-17 (Fig. 2a). The deepest sediments in this boring were brown clays and silts that appear to be undisturbed glacial loess. This was overlain by a thin lens of fine sand, which probably was deposited as in-channel sedimentation f a small stream. The fine-grained lithology at this site indicates that most of the sediments were deposited in flood plain and overbank environments. The bits of degraded plant material present in the layers of silty clay are consistent with this interpretation. Most of the site lacks the sandy lithology characteristic of in-channel sedimentation (Fig. 2b), indicating that overbank and flood-plain environments dominated at this site.

25 > 1 3 S	Lithologic Description
= =	= Brown clayey silt, sal core unel roots
-0-	chunks 12 lianite arranded
5++ = 1-	chunks of lignike arrounded by gray sitty clay
=	Brown sand and gravel
104	(water predicting)
70# 7====	= grayish green sitty alay
154	ENO HOLE
<u> </u>	· · · · · · · · · · · · · · · · · · ·

	meldures Lithologic Description
5f+	Brown clayey sitt, with lignite streaks Brown and gray clayey sitt
	Brown and gray clayeysilt
10++	Brown and gray chayey silt with lignise
15\$1	Brave and gray chyry silt
204	Distinct color change to gray plactic clay

Α

В

These fine-grained sediments are characterized by relatively low hydraulic conductivities. Extensive hydraulic testing, which included aquifer tests (ERC, 1990), indicated hydraulic conductivities on the order of 1 ft/day. The water-table surface at the site (measured on December 8, 1993; Figure 1) indicates that ground water moves onto the site from the east, and moves toward potential discharge areas in the drainage ditch n the south side of the Old Navy Road and in the marshy area to the north f the site. Because the site is almost entirely overlain by macadam (blacktop), vertical recharge to the water table is limited to the grassy area on the eastern border of the site.

The measured hydraulic conductivities and the water data allow rates f ground-water flow to be evaluated using Darcy's Equation:

$$v = (K dh/dx)/P$$
 (1)

where:

v is the average velocity of ground water in feet per day,
K is the average hydraulic conductivity in feet per day),
dh/dx is the hydraulic gradient (dimensionless), and
P is the sediment porosity (dimensionless).

The highest rates of ground-water flow occur in the eastern part of the site (fig. 1) where water levels decrease from about 269 ft to 265 feet above sea level over a lateral distance of about 200 ft. This gives a hydraulic gradient of 0.02. Given a hydraulic conductivity of 1 ft/d and an assumed

porosity of 0.3, which is typical of silty materials, a rough estimate of the average ground-water flow velocity is 0.067 ft/d. The lowest rates of ground-water flow occur near the center of the site where head declines are about 0.5 feet per 100 feet, or a hydraulic gradient of 0.005. These conditions indicate an average ground-water flow rate of 0.016 ft/d. Ground-water flow at this site probably occurs at rates that are intermediate between these two extremes. An average ground-water flow rate of about 0.03 ft/d, or about 10 ft/yr, is assumed to be representative f hydrologic conditions at this site. The data indicate that the closest potential point of contact for contamination transported by ground-water flow could be the drainage ditch on the south side of the Old Navy Road. Ground-Water Chemistry

Concentrations of TPH in ground water ranged from 52,000 µg/L to less than 100 μ g/L (Table 1). Two distinct plumes of contaminated ground water were observed. One plume was located near the buried storage tank near wells MEM-757-Bl, -B2, and -B3. Well MEM-757-B4 is directly downgradient of this plume and water from this well had hydrocarbon concentrations near the detection limit. Water from well MEM-757-6 is also downgradient of this contamination and contains low concentrations of contaminants. A separate contamination plume was present in the vicinity of the pumps and in the area of wells MEM-757-1, -2, -3, -7,-8, -12, -13, and -14.

Concentrations of dissolved oxygen, ferrous iron, and sulfide in ground water from the site are presented in Table 2. The water was generally aerobic, with the exception of wells B1 and B2, and contained very littl dissolved sulfide. Concentrations of ferrous iron were relatively high

Table 1.--Concentrations of Benzene, Toluene, Ethylbenzene, Xylene (total), and Total Petroleum Hydrocarbons (TPH) in ground water from monitoring wells at the Exchange Service Station, Naval Air Station Memphis, Tennessee, December 9, 1992.

[μ g/L, microgram per liter; TPH, Total Petroleum Hydrocarbons; R, replicate sample; A, dilution required and elevated the detection limit; <, less than]

	535 680	2,580	
MEM-757-B1 125 165	690	2,500	35,400
MEM-757-B2 2,810 595		2,890	28,100
MEM-757-B3 434 <20	252	487	10,500
MEM-757-B4 <2 <2	<2	5	107
MEM-757- 1 11,000 5,170	926	3,220	52,000
MEM-757- 2 3,680 430	230	1,160	23,200
MEM-757- 2R 4,600 527	302	1,470	27,500
MEM-757- 3 2,850 578	440	994	12,500
MEM-757- 4 <2 <2	<2	<4	<100
MEM-757- 4R <2 <2	<2	<4	<100
MEM-757- 5 <2 <2	<2	<4	<100
MEM-757- 6 ^h 165 - <20	27	<40	603
MEM-757- 7 · 115 105	265	2,190	2,680
MEM-757- 8 2,050 613	163	465	7,530
MEM-757- 9 <2 <2	<2	<4	<100
MEM-757-10 <2 <2	<2	<4	<100
MEM-757-11 5 <2	<2	<4	<100
MEM-757-12 4,240 603	255	696	10,000
MEM-757-13 11,700 3,570	710	2,080	24,100
MEM-757-14 14,000 5,820	1,130	4,020	24,200
MEM-757-15 <2 <2	<2	<4	<100
MEM-757-16 <2 <2	<2	<4	<100
MEM-757-17 <2 <2	<2	<4	<100
MEM-757-18 <2 <2	<2	<4	<100
MEM-757-19 <2 <2	<2	<4	<100

where contamination levels were high. Because ferrous iron is produced by microbial Fe(III) reduction (Lovley and others, 1989) this observation indicates some anaerobic microbial degradation of contaminants. The fact that hydrogen concentrations in the anaerobic wells are in the 0.2-0.3 range characteristic of microbial Fe(III) reduction (Chapelle and Lovley, 1992) is also consistent with contaminant degradation by Fe(III) reduction. The lack of dissolved sulfide (Table 2) and the relatively low concentrations f dissolved sulfate (Table 3) suggest that sulfate reduction is only a minor component in the microbial degradation of contaminants. The temperature f the water (Table 2) varied considerably, ranging from 14.2 to 20.4 C. The wells with the highest ground-water temperatures (MEM-757-1 through -14) are located in the center of the site and are overlain by macadam. Solar heating of the blacktop possibly has increased the ground-water temperature in the most contaminated areas.

Concentrations of nitrate and phosphate (Table 3) are relatively low at the site. The lack of nitrate precludes nitrate reduction as a significant microbial process in the degradation of petroleum hydrocarbons. Because nitrogen and phosphate are required by microorganisms to synthesize nucleic acids and proteins, microbial metabolism at this site may be limited by the lack of these nutrients.

There does not appear to be any correlation between the presence of contamination and concentrations of magnesium or calcium. There is, however, a distinct increase of bromide and chloride concentrations in the most contaminated ground water. This could reflect the use of bromine and chlorine catalysts during the manufacture of gasoline.

Table 2.--Dissolved oxygen, pH, temperature, ferrous iron [Fe(II)], sulfide [S²⁻], and hydrogen [H₂] measured in ground-water monitoring wells during VOC (volatile organic compound) sampling at the Exchange Service Station, Naval Air Station Memphis, Tennessee, December 9, 1992.

[mg/L, milligrams per liter; °C, degrees Celsius; nM, nanomolar; ND, no data collected; <, less than]</pre>

Well Number (see Fig. 1.2	Dissolved) oxygen¹	pH²	Temper- ature ³	Ferrous iron4	Sulfide ⁵	Hydrogen ⁶
1.	(mg/L)		(°C)	(mg/L)	(mg/L)	nM
MEM-757-B1	<0.1	6.13	15.2	18.0	<0.01	0.20
MEM-757-B2	<.1	6.15	17.5	17.5	<.01	.34
MEM-757-B3	.25	6.31	16.3	9.5	<.01	ND
MEM-757-B4	3.91	6.67	17.9	.6	<.01	ND
MEM-757- 1	.65	6.55	19.0	4.2	<.01	ND
MEM-757- 2	1.81	6.72	20.4	3.2	<.01	ND
MEM-757- 3	1.46	6.53	19.2	4.2	<.01	ND
MEM-757- 4	2.54	7.00	17.2	1.0	<.01	ND
MEM-757- 5	3.90	6.74	15.4	<.2	<.05	ND
MEM-757- 6	.91	6.24	17.8	2.2	<.01	ND
MEM-757- 7	1.00	6.46	18.2	5.3	<.01	ND
MEM-757- 8	3.52	6.56	18.6	3.2	<.01	ND
MEM-757- 9	3.02	6.90	16.5	1.0	· ND	ND
MEM-757-10	3.33	6.35	16.5	.5	<.01	ND
MEM-757-11	4.00	6.33	18.2	3.2	.40	ND
MEM-757-12	4.94	6.73	19.4	1.4	<.01	ND
MEM-757-13	3.79	6.48	19.7	1.0	<.01	ND
MEM-757-14	.99	6.34	17.8	3.4	<.01	ND
MEM-757-15	5.30	6.95	ND	.2	<.05	ND
MEM-757-16	4.80	6.35	15.4	.8	<.05	ND
MEM-757-17	3.20	6.38	16.5	2.0	<.01	ND
MEM-757-18	.98	6.70	14.2	1.2	ND	ND
MEM-757-19	3.75	6.85	14.3	1.0	<.01	ND

¹Dissolved oxygen was measured by using the Winkler titration technique.

²pH was measured by using a Beckmann⁷pH/temperature probe.

Temperature was measured by a Beckmann pH/temperature probe.

Ferrous iron was measured by using a Hach colorometric kit.

⁵Sulfide was measured by using a Hach colorometric kit. ⁶Hydrogen was measured by using reduction gas analyzer gas chromatography.

⁷ The use of trade names is for descriptive purposes only and does not constitute an endorsement by the U.S. Geological Survey.

Table 3.--Cations and anions in ground water from monitoring wells at the Exchange Service Station, Naval Air Station Memphis, Tennessee, December 9, 1992.

Well Number	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ 2-	Br ⁻	NO -	PO ₄ 3-
(see Fig. 1.	2) (mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	NO_3 (mg/L)	
(bee rig. r.	2) (mg/1)	(1119/11)	(1119/11)	(mg/b)	(1119/11)	(mg/L)	(mg/L)
							
MEM-757-B1	17.45	35.53	3.56	8.89	.01	1.86	<0.02
MEM-757-B2	28.47	50.00	1.60	1.24	.29	.05	<.02
MEM-757-B3	7.62	20.09	2.37	2.91	.09	.44	<.02
MEM-757-B4	30.58	40.00	2.27	6.71	.80	.74	<.02
MEM-757- 1	37.75	69.04	15.92	.64	1.99	.25	<.02
MEM-757- 2	26.41	61.38	4.49	1.31	.61	.14	<.02
MEM-757 -2R	NA	NA	4.61	1.27	.51	.02	<.02
MEM-757- 3	37.38	74.49	9.96	1.13	4.42	.03	<.02
MEM-757- 4	27.15	57.05	9.88	12.53	.14	.02	<.02
MEM-757- 4R	NA	NA	9.89	11.89	.12	.04	<.02
MEM-757- 5	23.50	38.87	4.16	7.13	.04	.47	<.02
MEM-757- 6	14.59	39.79	2.62	2.39	.40	.05	<.02
MEM-757- 7	41.28	78.79	32.08	.42	1.89	.02	<.02
MEM-757- 8	28.01 `	56.04	8.03	1.39	1.71	.17	<.02
MEM-757- 9	34.15	69.94	12.10	6.12	.78	.35	<.02
MEM-757-10	70.50	134.19	40.14	19.29	1.63	.20	<.02
MEM-757-11	60.14	121.02	10.35	8.12	1.62	.07	<.02
MEM-757-12	33.35	72.38	5.33	1.36	1.39	.01	<.02
MEM-757-13	38.28	66.71	8.97	.18	2.68	<.01	<.02
MEM-757-14	40.99	72.99	6.92	1.15	1.79	NA	<.02
MEM-757-15	68.09	88.06	3.91	6.12	1.45	.02	<.02
MEM-757-16	34.32	56.23	2.29	13.27	.86	2.04	<.02
MEM-757-17	39.23	74.34	4.96	25.03	.27	. 94	<.02
MEM-757-18	12.97	29.02	5.69	3.52	.04	.02	<.02
MEM-757-19	44.91	76.76	1.94	29.93	.09	2.05	<.02
			•				

Concentrations of the aliphatic organic acids formate and acetate (Table 4) were significantly higher in the most contaminated ground water relative to uncontaminated ground water at the site. This observation is important because organic acids are unstable intermediate products f hydrocarbon degradation by microorganisms and are not present in substantial concentrations in gasoline. Their presence at the site, therefore, is direct evidence that microorganisms were degrading petroleum hydrocarbons in situ. Similarly, concentrations of methane (Table 4) were significantly higher in contaminated ground water than in uncontaminated ground water. Again, because methane is a product of anaerobic microbial metabolism, this is direct evidence of microbial degradation of hydrocarbons at this site. There does not appear to be any correlation between concentrations of carbon dioxide (Table 4) and the presence of hydrocarbon contaminants.

Microbial Degradation Studies

The results of the laboratory BTX microcosm studies are shown in Figures 3, 4, and 5, respectively. The initial additions of BTX to the microcosms were calculated to provide a final concentration of 300 μ mol/L f each compound. The actual measured amounts in solution, however, were much lower and were about 150 μ mol/L for benzene (Fig. 3), 125 μ mol/L for toluene (Fig. 4) and about 110 μ mol/L for xylene (Fig. 5). The difference between the added compounds and what remained in solution suggests that a substantial proportion of these compounds is removed from solution and sorbed onto the aquifer materials. This observation, in turn, suggests that

Table 4.--Concentrations of the organic acids formate and acetate, and methane [CH₄] and carbon dioxide [CO₂] in ground-water monitoring wells at the Exchange Service Station, Naval Air Station Memphis, Tennessee, December 9, 1992.

[μ mol/L, micromoles per liter; mg/L, milligrams per liter; R, replicate sample; <, less than]

,				
Well Number (see Fig. 1.2)	Organ	ic Acids	Methane [CH4]	Carbon dioxide
.•	Formate (µmol/L)	Acetate (μmol/L)	(μmol/L)	[CO ₂] (mg/L)
MEM-757-B1	12.1	3.1	20.5	219.6
MEM-757-B2	1.2	. 1.6	65.4	312.0
MEM-757-B3	13.7	1.0	17.1	245.0
MEM-757-B4	2.8	<1.0	1.6	304.0
MEM-757- 1	8.5	74.0	832.9	246.1
MEM-757- 2	. 4	10.9	342.0	220.6
MEM-757 -2R	. 4	10.9	344.7	212.5
MEM-757- 3	3.2	15.0	571.8	235.2
MEM-757- 4	<1.0	<1.0	11.1	175.2
MEM-757- 4R	<1.0	<1.0	11.4	168.2
MEM-757- 5	1.2	<1.0	<1.0	139.7
MEM-757- 6	<1.0	<1.0	81.1	220.4
MEM-757- 7	3.6	1.0	310.4	247.0
MEM-757- 8	. 4	20.7	134.6	199.8
MEM-757- 9	<1.0	<1.0	1.7	226.2
MEM-757-10	<1.0	<1.0	<1.0	414.9
MEM-757-11	5.3	1.0	<1.0	414.3
MEM-757-12	<1.0	41.6	106.4	208.6
MEM-757-13	4.4	37.8	361.6	246.2
MEM-757-14	2.0	77.7	749.9	270.0
MEM-757-15	10.1	1.0	<1.0	411.3
MEM-757-16	1.0	1.0	<1.0	218.9
MEM-757-17	<1.0	<1.0	2.3	238.3
MEM-757-18	<1.0	<1.0	8.2	133.2
MEM-757-19	<1.0	<1.0	<1.0	271.1

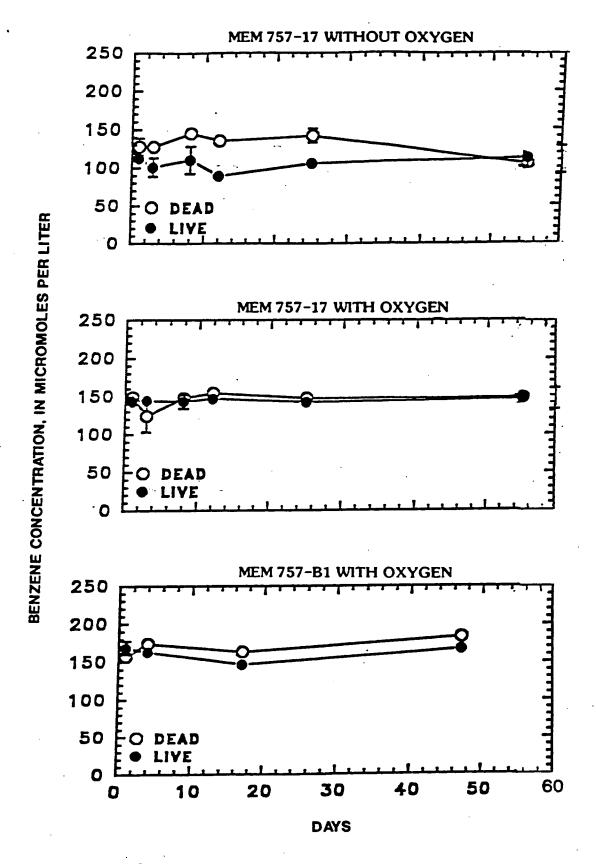


Figure 3.--Concentrations of benzene in triplicate microcosm experiments under anaerobic (without oxygen) and aerobic (with oxygen) conditions.

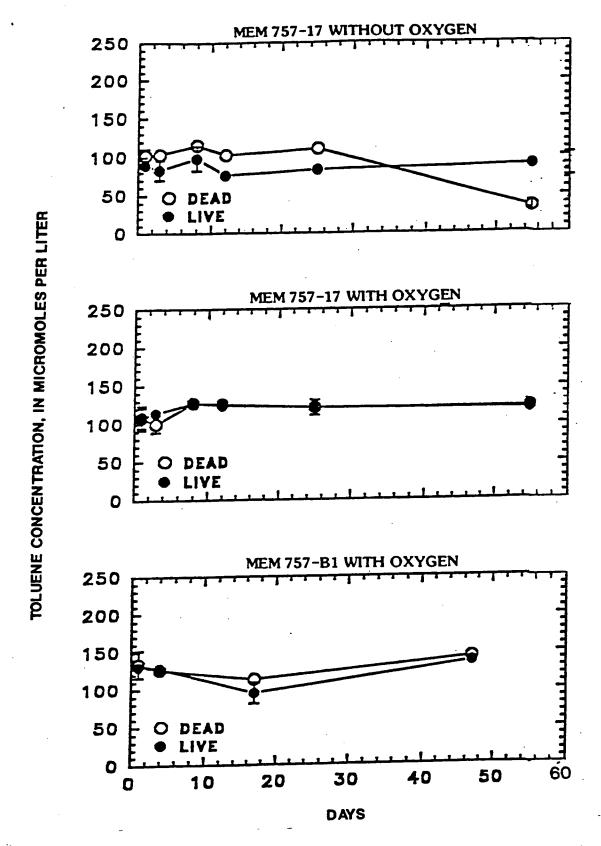


Figure 4.—Concentrations of toluene in triplicate microcosm experiments under anaerobic (without oxygen) and aerobic (with oxygen) conditions.

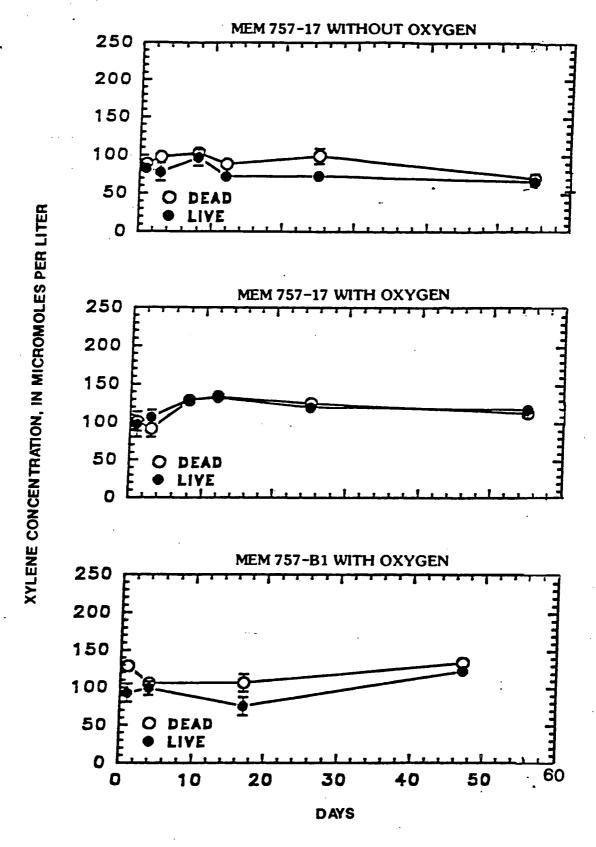


Figure 5.--Concentrations of xylene in triplicate microcosm experiments under anaerobic (without oxygen) and aerobic (with oxygen) conditions.

n n-biologic processes (that is, sorption) are important in retarding the movement of contaminants at this site.

Over the course of the experiment, no decreases in any of the BTX compounds relative to killed controls were observed in either the uncontaminated (MEM-757-17) or contaminated (MEM-757-B1) sediments. Furthermore, the presence of oxygen [+ 0₂] or the absence of oxygen [- 0₂] had no significant effect on degradative activity. However, some biologic activity in the samples was apparent because concentrations of CO₂ in live treatments (closed circles, Fig. 6) increased relative to killed controls (open circles, Fig. 6). Furthermore, mineralization of ¹⁴C-labeled glucose to ¹⁴CO₂ was observed in these sediments.

In order to assess the possibility that low but significant degradati n occurs in these sediments, a series of radiotracer studies were performed using ¹⁴C-labeled toluene. The results of these studies demonstrate that microorganisms in both the uncontaminated (MEM-757-17) and contaminated sediments (MEM-757-B1) are capable of degrading toluene. For example, in 9 days of incubation, about 5 percent of the added toluene was mineralized t ¹⁴CO₂ in the MEM-17 sediments (Fig. 7a). Similarly, about 30 percent of added toluene was mineralized to ¹⁴CO₂ in the MEM-757-B1 sediments in 9 days of incubation (Fig. 8a). Addition of nitrogen and phosphate did not significantly increase toluene degradation (Fig. 7b) relative to non-amended treatments (Fig. 7a) in the uncontaminated MEM-757-17 sediment. In the contaminated sediment, addition of nitrogen and phosphate actually depressed production of ¹⁴CO₂ (Fig. 8b) relative to non-amended treatments (Fig. 8a).

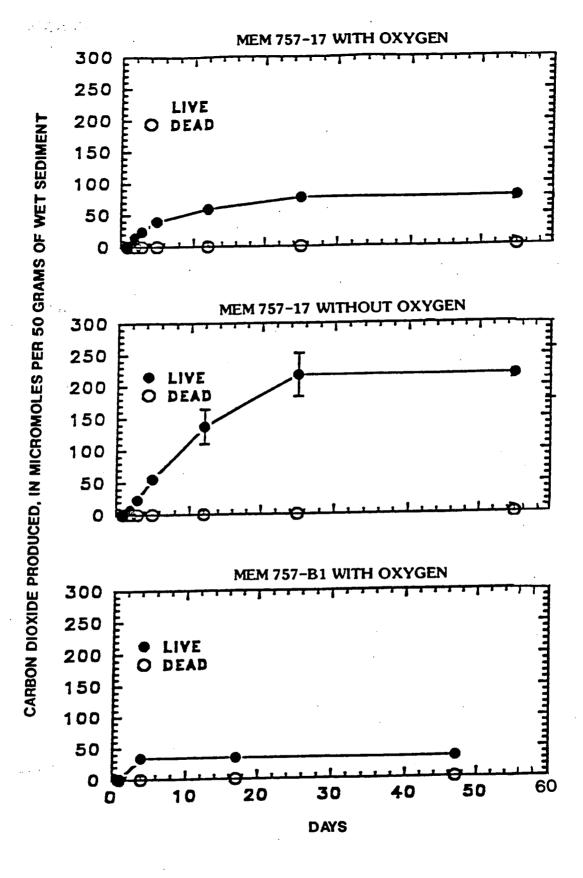


Figure 6.--CO₂ production in anaerobic (without oxygen) and aerobic (with oxygen) microcosms.

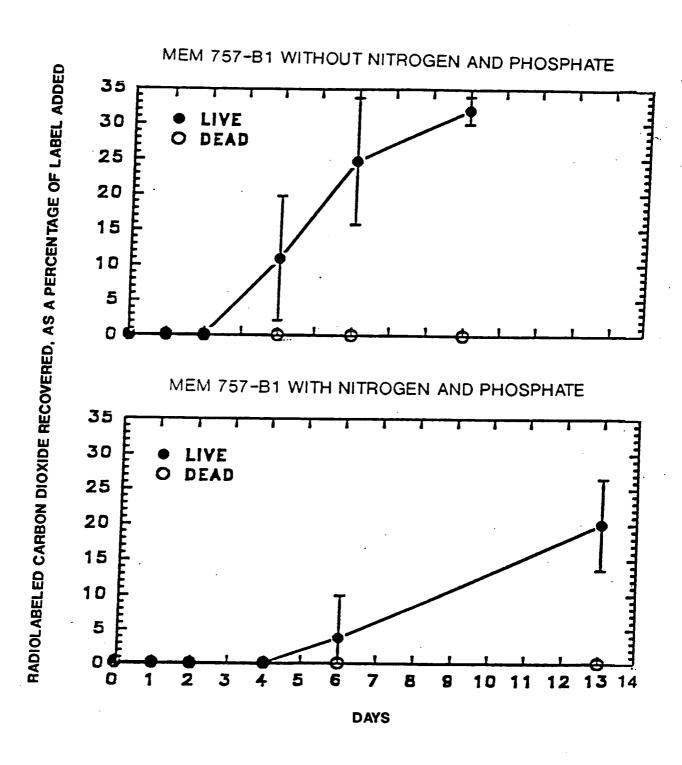


Figure 7.—Production of ¹⁴CO₂ from ¹⁴C-labeled toluene in contaminated sediments with and without the addition of nitrogen and phosphate. Data points are means +/- standard deviations for triplicate microcosms

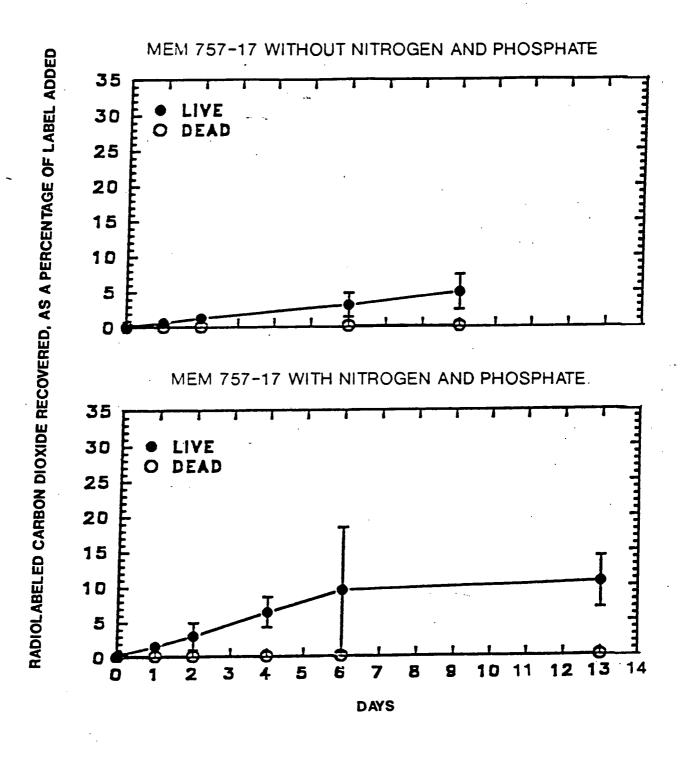


Figure 8.--Production of ¹⁴CO₂ from ¹⁴C-labeled toluene in contaminated sediments with and without the addition of nitrogen and phosphate. Data points are means +/- standard deviations for triplicate microcosms

Although degradation was evident using the radiotracer method, degradation was not evident using the microcosm method. These results do not indicate disagreement between the two experiments, but rather reflect the sensitivity of the methods. The radiotracer studies indicate a toluene transformation rate of about $10^{-4} \, \mu \text{mol gm}^{-1} \text{sediment day}^{-1}$. In 50 days, about 0.25 μmol of toluene would be transformed by the 50 grams of sediment present in the microcosms. This is far too small a change to be detected by HPLC analysis. Thus, the results of these experiments are consistent with each other and indicate that microbial degradation of toluene occurs at this site, but that the rates are low.

DISCUSSION

Distribution of Contaminated Ground Water

The distribution of contaminated ground water at this site indicates that the history of the site is more complex than previously thought. There are two plumes of contamination in the area that are chemically distinct from each other. The UST plume is centered around wells MEM-757-B1 and MEM-757-B2 and is characterized by relatively high concentrations of xylene and lower concentrations of benzene and toluene. The plume centered around the pump island is characterized by high concentrations of benzene and toluene, but lower concentrations of xylene.

The data indicate each plume encompasses a radius of about 50 ft and that the concentration gradients between the plumes and the surrounding uncontaminated are very sharp. For example, concentrations of the following the surrounding uncontaminated are very sharp.

TPH, benzene, and xylene at well MEM-757-B3 are 10,500, 434, and 487 μ g/L respectively. Fifty feet downgradient of this site at well MEM-757-B4, however, contaminant levels were 107 μ g/L TPH, < 2 μ g/L benzene, and 4 μ g/L xylene. A similar sharp boundary between contaminated and uncontaminated ground water occurs at the PI plume. Furthermore, this sharp boundary has apparently been maintained over a number of years because the distribution of contaminated ground water has not changed significantly since 1987 (Fig. 9). Because ground water is assumed to be moving an average of about 10 ft/yr at the site, the lack of observed contaminant movement indicates that contaminants are being retarded relative to the flow of ground water.

Field Evidence for Microbial Degradation of Hydrocarbons

The ground-water chemistry data provide several lines of evidence that petroleum hydrocarbons are being degraded in situ. Methane and ferrous iron are final products of microbial methanogenesis and Fe(III) reduction, respectively. The relatively high concentrations of these constituents in the highly contaminated zones, therefore, are consistent with ongoing methanogenesis and Fe(III) reduction. More importantly, the presence of relatively high concentrations of acetate and formate (Table 4) in the contaminated zones indicates microbial transformation of petroleum hydrocarbons.

The presence of dissolved ferrous iron, methane, and dissolved oxygen indicates that several aerobic and anaerobic microbial processes are ongoing at this site. Where dissolved oxygen is present in the ground water, aerobic degradation of petroleum hydrocarbons will predominate. When

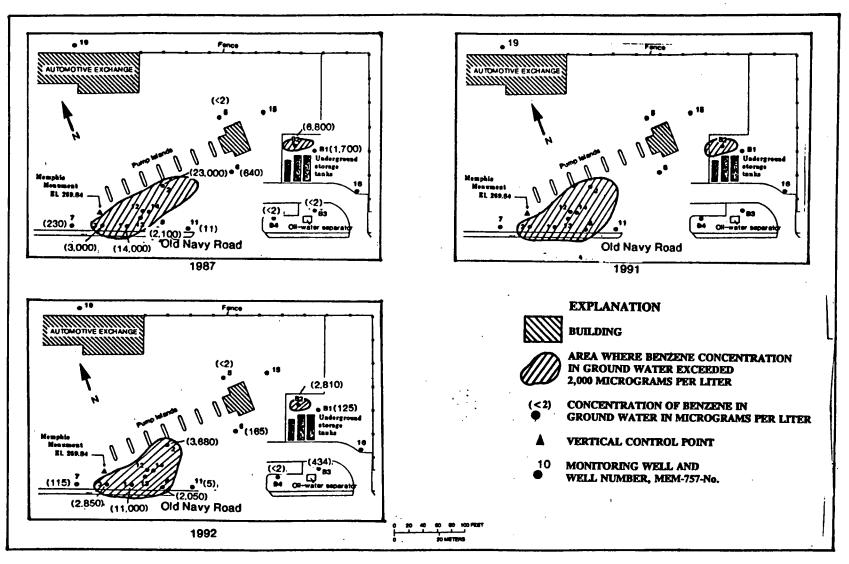


Figure 9.—Ar as where concentrations of benz ne in ground wat r at the Naval Exchange Service Station site exceeded 2.000 micrograms per liter, 1987–1992. (Modified from Harding Lawson Associates, 1987; ERC Environmental and

Energy Services Company, 1990, 1991)

dissolved oxygen is exhausted, anaerobic degradation will commence. Under anaerobic conditions, Fe(III) reduction will be the preferred process until available Fe(III) in the sediment has been exhausted. When Fe(III) is n longer available, methanogenesis will be the preferred process. The field data show that at the UST plume, ferrous iron concentrations are relatively high and methane concentrations relatively low. This suggests that Fe(III) reduction is the predominant anaerobic process at the UST plume. In the plume centered around the pump islands, concentrations of methane are relatively high and ferrous iron relatively low, indicating that Fe(III) has been exhausted and that methanogenesis is the predominant anaerobic process. This difference between the two plumes is significant and may indicate that the contamination in the area of the pump islands preceded the contamination at the underground storage tanks.

Estimates of contaminant biodegradation rates can be made based in observed concentration declines along ground-water flowpath segments. For example, between well MEM-757-B3 and MEM-757-B4, benzene concentrations decrease from 434 to <2 μ g/L. Given a flowpath segment length of 50 feet and a ground-water flow rate of 10 ft/year, a benzene degradation rate can be calculated from the equation

$$D_r = \Delta Benzene R_{gw}/L_{fp}$$
 (2)

where

 D_r is the estimated degradation rate, $(\mu g/L^{-1}yr^{-1})$

 $\Delta Benzene$ is the change in benzene concentration over the flowpath segment, $(\mu g/L^{-1})$

 R_{gw} is the rate of ground water flow, (feet/yr), and

 L_{fp} is the length of the flowpath segment (feet). In this case, D_r for benzene is calculated to be 86.6 $\mu g L^{-1} yr^{-1}$ (1.1 μM $L^{-1} yr^{-1}$). Similar estimates can be made for toluene degradation rates. For example, on the flowpath segment between well MEM-757-B2 and MEM-757-15, toluene concentrations decrease from 595 to < 2 $\mu g/L$. Given a L_{fp} f 50 feet, Atoluene of 595, and an R_{gw} of 10 ft/yr, D_r for toluene is estimated to be 119 $\mu g L^{-1} yr^{-1}$ (1.3 $\mu M L^{-1} yr^{-1}$). These estimates are subject t error as a result of (1) not incorporating the effects of hydrodynamic dispersion, and (2) not including the effects of sorption.

Laboratory Estimates of Toluene Degradation Rates

The radiotracer studies can be used to estimate rates of toluene degradation in this system. In 9 days of incubation of the contaminated MEM-757-B1 sediments, approximately 30 percent of the added ^{14}C -toluene was mineralized to $^{14}\text{CO}_2$ (Fig. 8), indicating a first-order degradation rate constant of (0.3/9), or $0.033~\text{d}^{-1}$. The concentration of toluene in the experimental vials was 25 μ mol/L, which gives a toluene degradation rate f 25 x $0.033 = 0.825~\mu$ mol L $^{-1}\text{d}^{-1}$, or 301 μ mol L $^{-1}$ yr $^{-1}$. This experimentally-determined degradation rate is much faster than the rates estimated using field data. However, it is commonly observed that laboratory incubations tend to overestimate degradation rates.

Hydrologic and Micr biologic Containment of Contamination

Field and laboratory evidence indicates that natural hydrologic and microbiologic processes serve to contain the BTEX contamination at this site. The field data, which includes BTEX measurements made from 1986 t 1992, show that contamination movement is severely restricted. If transport of BTEX was entirely conservative, concentrations in ground water downgradient of the contaminated zones (such as wells MEM-757-B4, MEM-757-15, MEM-757-9, and MEM-757-10) would be in the hundreds r thousands of μ g/L, based on rates of ground-water flow. Instead, observed concentrations are near or below detection limits. These observations are consistent with ambient rates of ground water flow and laboratory-m asured rates of toluene degradation.

The one-dimensional transport of a reactive solute by flowing ground water is described by the equation

$$\partial C/\partial t = D \partial^2 C/\partial x^2 - v \partial C/\partial x - kC$$
 (3)

where

C is concentrations of solute, in micrograms per liter,

x is distance in feet,

D is the diffusion coefficient in feet squared per day,

v is the velocity of ground water flow in feet per day, and

k is degradation rate constant in day-1.

After steady-state conditions are attained as time gets large, concentration changes with time become small and the equation simplifies to

$$D d^{2}C/dx^{2} - v dC/dx - kC = 0$$
 (4)

This is an ordinary differential equation that can be solved given appropriate boundary conditions. For boundary conditions

and

$$C \longrightarrow 0$$
 as $x \longrightarrow \alpha$

the solution is

$$[v - \sqrt{v^2 + 4Dk})/2D] =$$

$$C(x) = C_0 \exp$$
 (5)

If the range of parameters determined at this site from field and laboratory studies are applied to this equation, estimates of contaminant concentration decreases with distance from the source can be calculated. For the range of experimentally determined degradation rate constants (k ~ 0.016 d⁻¹) and ground-water flow velocities (v = 0.03 to 0.067 ft/d), a diffusion coefficient characteristic of silty clays (D = 0.038 ft²/d), and a constant contaminant source ($^{\circ}$ C) of 1,000 $^{\mu}$ G/L, calculated concentration profiles for this range of ground-water velocities are:

v = 0.03 ft/d

v = 0.067 ft/d

x (ft)	Concentration µg/L	x (ft)	Concentration µg/L
0	1,000	,O	1,000
1	694	1	808
5	161	5 .	[*] 345
10	25	10	118
15	4.2	15	40
20	0.67	20	14
25	0.10	25	4.9

Clearly (Fig. 10), as ground-water flow rates increase, the length of the flowpath segment required to remove BTEX also increases. However, f r the range of ground-water flow rates found at the site, it appears that most contaminants will be removed over a flowpath segment of between 20 and 30 feet.

Although such an analytical equation is inherently simplistic, it does illustrate why observed concentration gradients at this site are so sharp. The combination of low ground-water velocities with ambient biodegradation rates effectively confines dissolved contaminants to within 20 to 30 ft f the contamination sources. This analysis indicates that transport of dissolved contaminants to the nearest possible point of contact with human beings, the drainage ditch on the south side of Old Navy Road (100 feet from the contaminants), is unlikely.

Effectiveness of Enhanced Bioremediation Relative to Non-Enhanced Bioremediation

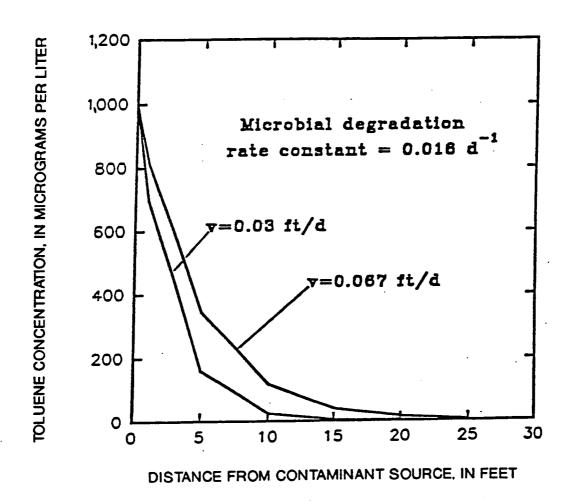


Figure 10.-Calculated concentration profiles for toluene given a constant biodegradation rate and varying rates of ground-water flow.

The laboratory studies do not indicate that attempts to enhanc bioremediation by addition of nitrogen and phosphate will significantly increase biodegradation rates. In the uncontaminated MEM-757-17 sediments, there was greater mineralization of toluene with nitrogen and phosphate addition relative to the unamended treatments, but these effects were minimal. In the contaminated MEM-757-Bl sediments, nutrient additi n did not stimulate ¹⁴CO₂ production. Thus, these experiments provide no clear evidence that the addition of nitrogen and phosphate would have any significant advantage over non-enhanced degradation rates.

CONCLUSIONS

Available hydrologic, geochemical, and microbiologic evidence indicates that naturally occurring microbial populations at the Naval Exchange Sit are actively degrading petroleum hydrocarbons. Rates of degradation are slow. However, because movement of ground water at this site is also slow, dissolved contaminants have been restricted to within 20 or 30 ft f the contaminated sediments. Because the nearest possible point of contact with humans (the drainage ditch on the south side of Old Navy Road) is about 100 ft upgradient from the contaminated sediments, the chances of human exposure to the contamination are small. There is no clear evidence that addition of nitrogen and phosphate nutrients will significantly enhance biodegradation rates.

This study is significant because it provides a clear example f how even slow rates of biodegradation can act to confine plumes of petroleum-hydrocarbon contamination. Rates of ground-water flow are unusually 1 w at the Naval Exchange site. However, because rates of ground-water flow ar less than rates of biodegradation, soluble contaminants are effectively confined and do not move off site.

REFERENCES

- Barker, J.F., G.C. Patrick, and D. Major, 1987, Natural attenuation f aromatic hydrocarbons in a shallow sand aquifer. <u>Ground-Water</u>

 <u>Monitoring Review</u>, Winter, pp. 64-71.
- Chapelle, F.H. and D.R. Lovley, 1992, Competitive exclusion of sulfate reduction by Fe(III)-reducing bacteria: A mechanism for producing discrete zones of high-iron ground water. Ground Water 30(1):29-36.
- ERC Environmental and Energy Services Company, 1990, Vacuum extraction pil t study and remedial investigation report, volume 1.
- Harding Lawson Associates, 1987, Site Characterization Study, Naval Exchange Service Station, NAS Memphis.
- Harding Lawson Associates, 1988, Final Remedial Action Plan (RAP), Naval Air Station Navy Exchange (NX) Service Station, Millington, Tennessee.
- Lovley, D.R. M.J. Baedecker, D.J. Lonergan, I.M. Cozzarelli, E.J.P.

 Phillips, and D.I. Siegel, 1989, Oxidation of aromatic contaminants

 coupled to microbial iron reduction, Nature 339:297-299.
- Skougstad, M.W., M.J. Fishman, L.C. Friedman, D.E. Erdman, and S.S. Duncan, 1978, Methods for analysis of inorganic substances. <u>U.S. Geological</u>

 <u>Survey Open-File Report 78-679</u>, 626 p.

APPENDIX B

EVALUATION OF VACUUM EXTRACTION AS A REMEDIATION OPTION



2. Another area displaying high TPH concentrations was identified around the active tank pit area. A third area displaying high concentrations of TPH was near building 341 and adjacent to Old Navy Road. A review of old site plans indicate 3 UST's were abandoned in place in this area 21 years ago. It is not known if these tanks were removed during subsequent road construction activities.

A ground water pump test was performed to determine the hydraulic characteristics of the aquifer at subject site. The test results indicated that calculated transmissivities and storativities ranged from 0.003504 to 0.001933 ft²/min. and 0.0113 to 0.00212 ft²/min. respectively. Calculations projected 5.4 feet of drawdown at 2 feet from a 6-inch diameter well, screened 30 feet into the unconfined aquifer, pumping at a rate of 0.37 gpm.

An option considered for the remediation of soils contaminated with gasoline is vapor extraction. A series of air pump tests at high, medium, and low vacuum pressures with select observation wells closed then opened was performed. Well MEM-757-12, the same 6-inch well used for pumping in the ground water pump test, was used as a vapor extraction well. Also, well MEM-757-14, a 4-inch diameter well, was used as an extraction point in a second series of tests. Both extraction wells and the 2 nearest observation wells were equipped with well seals and ground water pumps to expose as much soil to venting as possible. Extraction well head pressures, vapor recovery flow rates, and monitoring well pressures were recorded and used to develop design variables for a remedial system, should vapor extraction be determined applicable.

Subsurface soil temperature at depths of 3.7, 7.7, and 16.5 feet below surface grade averaged 81,71, and 67°F respectively. Temperature, barometric pressure, and static pressures within the observation wells (no vacuum applied) were reviewed. No distinct pattern in fluctuations was correlated. Therefore, observation well pressure readings were not corrected.

Flow rates observed during the tests were higher than expected and required correction. Maximum sustained flow rates for the 6-inch and 4-inch diameter wells were 8.6 and 7.1 scfm at 90 and 100 inches of water yielding 4.2 and 8.6 feet radii of influences respectively. The larger radius of influence calculated for MEM-757-14 was attributed to the irregular saturated soil profile around the extraction wells.

Calculations derived from the ground water pump test indicate desaturating the soil zone, most highly concentrated with petroleum hydrocarbons, sufficiently to utilize vacuum extraction would require approximately 1,100 ground water recovery wells. Installation and maintenance costs incurred with a ground water recovery and vacuum extraction system of this complexity prevents vacuum extraction from being a practical remedial option.

APPENDIX C

HARDING LAWSON ASSOCIATES EVALUATION OF BIODEGRADATION

AS A REMEDIATION OPTION

V BIODEGRADATION INVESTIGATION

A. <u>Introduction</u>

The presence of an indigenous population of microorganisms that can utilize hydrocarbon for growth has been observed in many types f leak/spill situations on soil, in surface water, and in groundwater. A recent and innovative technique for aquifer remediation involves stimulating the indigenous microflora to degrade subsurfac contaminants. Stimulation of these native microorganisms can result in the complete destruction of the contaminants, whereas chemical or physical treatment may result in incomplete destruction or transfer f the contaminant to another phase within the environment. Biostimulation is often achieved by the addition of nutrients (electron acceptors and inorganic nutrients) that are limited in the presence f high contaminant concentrations. Field investigations over the past fifteen years have shown that the conditions necessary to establish a maximum rate of degradation varies from aquifer to aquifer. It was, therefore, necessary to conduct laboratory studies to evaluate the specific characteristics of the aquifer in order to obtain information concerning the nutrient supplements required to optimize biodegradation.

In laboratory microcosm studies, representative soil and groundwater samples from the contaminated site that contain the indigenous microorganisms are supplemented with various concentrations of nutrients known to be required for growth by hydrocarbon-utilizing microorganisms. Over the appropriate incubation period, the microbial populations and organic contaminant profiles are monitored periodically to evaluate the degree of hydrocarbon degradation achievable in the samples. Following the study, a nutrient formulation for stimulating the indigenous microorganisms is recommended for the full-scale implementation of the bioremediation program.

This section presents the findings of our laboratory study of the potential for biodegradation of hydrocarbon present in the soil and groundwater at the NX Service Station.

The purpose of the study was to evaluate the feasibility of aerobic biodegradation of hydrocarbon (gasoline) contamination in soil and groundwater at the site. The laboratory study was designed to:

- Enumerate the existing bacterial populations capable f degrading the contaminants in soil and groundwater at the project site
- Evaluate the existing potential for the petroleum hydrocarbon in soil and groundwater at the project site to be biodegraded

Evaluate and recommend th supplemental nutrients needed to optimize biological degradation.

• Evaluate the biodegradation potential for the contaminants in soil and groundwater under enhanced conditions.

B. Field and Laboratory Methods and Procedures

Soil and Groundwater Sampling

Soil and groundwater samples were collected for two purposes:

(1) to characterize significant hydrocarbon contamination in soils and groundwater, and (2) to generally characterize inorganic geochemistry of shallow soils and groundwater. Samples from MEM-757-1, MEM-757-2 and MEM-757-SB-1 were collected primarily to characterize hydrocarbon contamination. Samples from MEM-757-7 through MEM-757-9 were collected primarily to characterize the general geochemistry of shallow soils and groundwater at the site.

Eight-liter water samples were collected from the following monitoring wells at the site:

- MEM-757-1
- MEM-757-2
- MEM-757-7
- MEM-757-8
- MEM-757-9

Additionally, three disturbed soil samples, weighing approximately two kilograms each, were collected from the following borings:

- MEM-SB-1, 5 to 10 feet
- MEM-757-8, 8.5 to 10 feet
- MEM-757-9, 13.5 to 15 feet

Refer to Appendices B-1 and B-4 for detailed descriptions of soil and groundwater sampling methods and procedures.

2. Chemical Analyses

Organic chemical profiles, which included total light hydrocarbon (TLH) and (BTX) were developed for each soil and groundwater sample. Inorganic geochemical profiles, which included nitrogen as ammonia and nitrate, phosphate as orthophosphate, carbonate, sulfate, bicarbonate, total alkalinity (as CaCO₃), pH, dissolved iron, manganese, magnesium, calcium, and potassium were determined for each groundwater sample. Inorganic geochemical profiles, which included nitrogen as ammonia and nitrate, phosphate as orthophosphate, carbonate, sulfate, pH, available iron, manganese, magnesium, calcium, and potassium were also developed for each soil sample. Refer to Appendix C-1 for descriptions of laboratory analytical methods and procedures.

All organic and inorganic chemical profiles for soil and groundwater samples were performed by a laboratory certified by the State of California to perform chemical analyses of hazardous materials.

3. <u>Microbiological Analyses</u>

Each groundwater and soil sample was analyzed to estimate the total heterotrophic microbial population and the microbial population capable of utilizing hydrocarbon (gasoline) as a sole source of carbon and energy.

Hydrocarbon (gasoline) utilizers were estimated by an adaptation of a most probable number (MPN) technique to enumerate hydrocarbon utilizers from environmental soil and water samples (Mills and Colwell, 1978). Refer to Appendix C-2 for detailed descriptions of laboratory analytical methods.

4. Soil and Groundwater Microcosms

Soil and groundwater microcosms were prepared to observe the effectiveness of heterotrophic microbial populations on the breakdown of hydrocarbon (gasoline) contaminants. A two-liter groundwater sample obtained from Well MEM-757-2 was utilized to prepare 36 groundwater microcosms that were divided equally into the following groups:

- Normal no nutrient or biological supplements
- Enhanced nutrients added to stimulate the indigenous biological activity
- Abiotic sodium azide added to prevent biological activity

Silty clay and clayey silt soils contaminated with hydrocarbon (gasoline) from various depths in two borings, MEM-757-8 and MEM-757-SB1, were used in this evaluation. The soil sample used for each microcosm group was thoroughly mixed prior to preparation of the microcosms. Thirty-six microcosms were prepared and divided into the groups described above. Refer to Appendix C-3 for detailed descriptions of laboratory analytical methods and procedures f r preparation and testing of the soil and groundwater microcosms.

Organic chemical analyses for TLH and BTX and microbiological analyses for populations were performed during the treatability study on soil and groundwater microcosms using the same analytical methods described in Appendices C-1 and C-2.

C. Data Analysis and Interpretation

1. Microbial Population

Results of the microbial evaluation of soil and groundwater samples collected at the NX Service Station are summarized in Tabl 7. The evaluation estimated the total number of heterotrophic

TABLE 7

Enumeration of Total Heterotrophic and Gasoline-Utilizing Microorganisms in Soil and Groundwater Samples NX Service Station, NAS Memphis

Sample Location	Sample Type	Total Heterotrophic Microorganisms	Gasoline-Utilizing Microorganisms
MEM-757-1	water	9,500 CFU/ml	170 CFU/ml
MEM-757-2	water	7,900 CFU/ml	1,600 CFU/ml
MEM-757-7	water	690,000 CFU/ml	5,400 CFU/ml
MEM-757-8	water	980,000 CFU/ml	16,000 CFU/ml
MEM-757-9	water	960,000 CFU/ml	3,500 CFU/ml
MEM-757-SB	-lsoil	3,600 CFU/gram	79 CFU/gram
MEM-757-8	soil	6,100 CFU/gram	33 CFU/gram
MEM-757-9	soil	9,000,000 CFU/gram	12 CFU/gram

Note: CFU = Colony-forming units

microorganisms per sample and, of these, the microorganisms that have the metabolic capability to utilize hydrocarbon (in this case, gasoline) as a primary source of carbon and energy.

Although there is considerable variation in the size of the microbial population throughout the site, microorganisms capable of degrading the contaminants present at the site were observed at every sample location. The percentage of gasoline-utilizers as a portion of the total heterotrophic population ranges from 0.0001% (MEM-757-9, soil) to 20 percent (MEM-757-2, groundwater).

Groundwater samples having the highest concentration of organic contaminants generally had a reduced total heterotrophic population but a substantial gasoline-utilizing microbial population. This distribution could be a result of toxicity and contaminant selective pressures exerted on the microbial population. These pressures lower the total microbial population while selecting for those organisms (gasoline utilizers) that are tolerant of and/or have the ability to degrade the contaminants, thus increasing their population. This selection process would account for the higher gasoline-utilizer population in samples with high concentrations of contaminants. Samples with low concentrations of contaminants (MEM-757-9, soil) have relatively little selective pressure that affects the total microbial population and the gasoline utilizers constitute a very small percentage of the total population.

The results indicate that the existing microbial population contains a subpopulation of microorganisms capable of utilizing gasoline as a primary source of carbon and that this subpopulation is distributed throughout the project site. This gasoline-utilizing microbial population is the segment of the total microbial population that would be stimulated in a biorestoration program.

2. Microenvironmental Factors

Previous biodegradation studies at various sites have indicated that even in the presence of adapted microorganisms with the metabolic capability to degrade subsurface hydrocarbon contaminants, factors such as lack of essential nutrients, substrate inaccessibility, pH, temperature, and the presence of toxicants can limit hydrocarbon degradation by these microorganisms.

The results of inorganic analyses of the groundwater and soil samples are summarized in Table 8. Analytical results for the groundwater samples indicate that several inorganic nutrients required for microbial degradation, namely nitrogen, phosphorus, and dissolved iron, are present throughout the project site only in very low concentrations or are below the detection limit of the analytical method, thus probably limiting the microbial metabolism of the hydrocarbon in the groundwater.

Geochemical Results of Groundwater Analyses
NX Service Station, NAS Memphis

TABLE 8

					
Parameter	Well MEM-757-1	Well MEM-757-2	Well MEM-757-7	Well MEM-757-8	Well MEM-757-
PH	7.0	6.9	7.2	7.0	7.1
Ammonia-N	ND	ND	ND	ND	ND
Nitrate-N	ND	ND	ND	ND	ND
Orthophosphate-P	2.0	1.3	2.2	2.6	1.3
Carbonate	ND	ND	ND	ND	ND
Sulfate	10	13	12	13	44
Dissolved Iron	ND	ND	. ND	ND	ND
Dissolved Manganese	2.6	3.7	1.1	1.7	0.52
Dissolved Magnesium	39	24	33	39	43
Dissolved Calcium	72	55	68	74	98
Dissolved Potassium	1	1	1	1	1
Bicarbonate	500	390	440	540	510
Total Alkalinity (as CaCC ₃)	410	320	360	440	420

Notes:

All analytical results are reported in mg/l except pH which is in standard units.

ND Not Detectable

The results of inorganic analyses f the soil samples are summarized in Table 9. The inorganic analyses for soil indicat that these inorganic nutrients (nitrogen, phosphorus, and available iron) may also probably be limiting microbial degradation of the hydrocarbon in the soil environment. Although substantial nitrogen is present in the soil as ammonia, most of the ammonia may not be readily available for the microorganisms to use in metabolizing the hydrocarbon. A larg percentage of the ammonia could be adsorbed to clays present in the soil and/or adsorbed by organic matter present in the soil. Additionally, environmental conditions in the subsurface are not conducive t transforming ammonia to nitrogen that is available for metabolism of the hydrocarbon.

Phosphorus, analyzed as orthophosphate in the soil, was not detected (detection limit: 4 mg/kg) at locations MEM-757-SB-1 or MEM-757-8; however, phosphorus was detected at MEM-757-9 (17 mg/kg) in a sufficient concentration to promote microbial growth. These results indicate that the lack of phosphate in locations with high contaminant concentrations and the disparate distribution of phosphate at the project site could potentially limit microbial degradation of the hydrocarbon present in the soil.

TABLE 9

Geochemical Results of Soil Analyses
NX Service Station, NAS Memphis

Parameter	Boring MEM-757-SB-1	Boring MEM-757-8	Boring MEM-757-9
рн	8.4	7.9	7.9
Ammonia-N	60	80	140
Nitrate-N	1	2	ND
Orthophosphate-P	ND	ND	17
Carbonate	12	ND	ND ·
Sulfate	ND	3	9.5
Available Iron	ND	ND	ND
Available Manganese	170	130	65
Available Magnesium	620	560	360
Available Calcium	1,400	1,400	2,000
Available Potassium	40	40	40

Notes: All analytical results are reported in mg/kg except pH which is in standard units.

ND - Not Detectable

Iron, analyzed as dissolved ir n in the groundwater (detection limit: 1 mg/l) and available iron in the soil (detection limit: 2 mg/kg), was not detected in any of the samples analyzed. Microorganisms require iron as a micronutrient to metab lize hydrocarbon. The lack of iron in the soil and groundwater could potentially limit microbial degradation of the hydrocarbons.

The results indicate that stimulation of the indigenous microbial population in the soil and groundwater to metabolize the hydrocarbon present would require the addition of the following:

- Nitrogen as a nitrate salt
- Phosphate as a potassium salt
- Iron as a ferric salt
- Oxygen.

The acceptable concentrations of micronutrients required to enhance microbial metabolism are:

- nitrogen 20 milligram (mg) per 100 mg hydrocarbon
- phosphorus 5 mg per 100 mg hydrocarbon
- iron 1 mg/l.

3. Treatability Study

Soil and groundwater microcosms were constructed in a laboratory treatability study utilizing site material to demonstrate the existing potential for microbial degradation of the hydrocarbon

(gasoline) and the potential f r increasing microbial degradation through biostimulation. The concentration data for each sampling point during the treatability study were expressed as the mean of three replicate microcosm analyses. Table 10 summarizes percentages f TLH and total BTX removal in the soil and groundwater microcosms under various treatment conditions during the study period. Plate 16 is a comparison of the total heterotrophic and gasoline-utilizing microbial populations in the normal and enhanced microcosms. heterotrophic population in the enhanced microcosm increased by greater than four orders of magnitude during the incubation period; the gasoline-utilizing population increased by greater than two orders of magnitude. The increase in the two microbial populations is concurrent with the disappearance of contaminants, indicating active utilization of the hydrocarbon contaminants as a source of carbon and energy. Th total heterotrophic and gasolineutilizing populations in th normal microcosms did not increase significantly during the incubation period. The total heterotrophic population in the normal microcosms did increase approximately one order of magnitude during the final week of the study. However, the gasoline-utilizing population remained constant, suggesting that the increase in the total heterotrophic population was not a direct result of hydrocarbon utilization.

TABLE 10

Percentage of Total BTX and TLH Loss After Incubation Under Various Treatment Conditions NX Service Station, NAS Memphis

	Treatment Conditions					
	Groundwater		Soil			
	Normal	<u>Abiotic</u>	Enhanced	Normal Normal	Abiotic	Enhanced
Total BTX (1 TLH (2)) ₈	. 5	99.8	92	79	99
	10	35	98	62	64	92

Note:

- (1) Total Benzene, Toluene and Xylene.
- (2) Total Light Hydrocarbon.

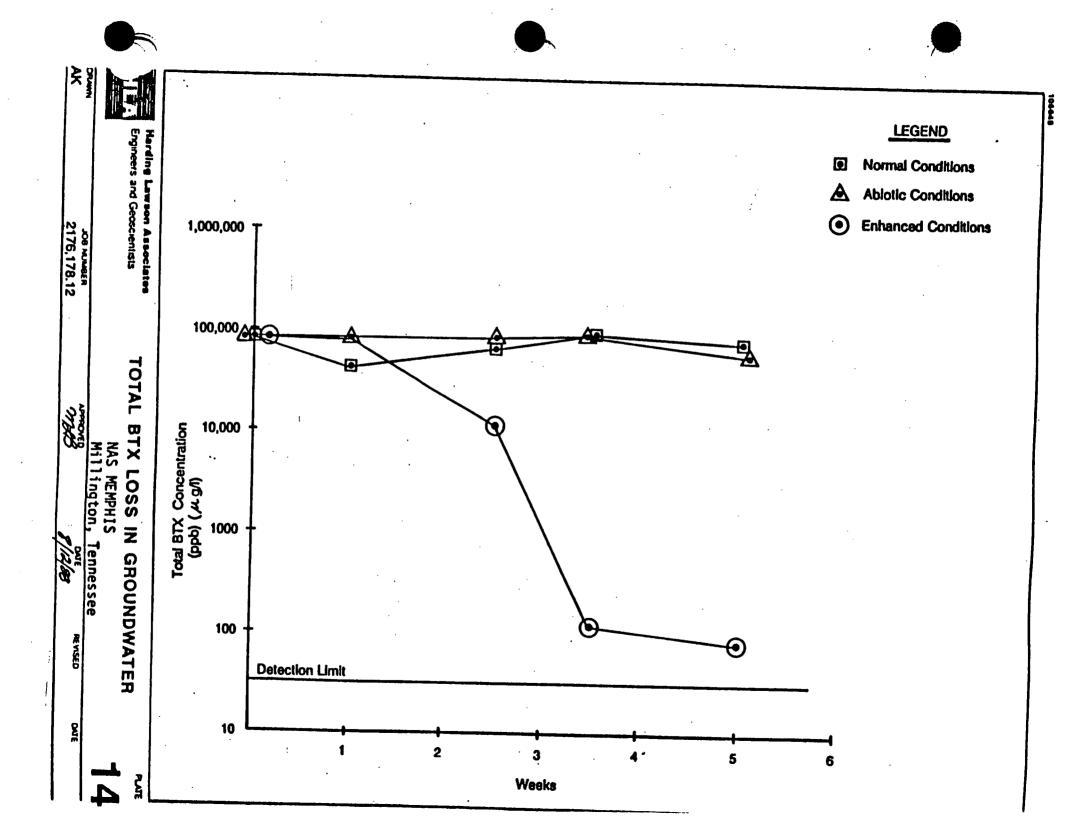
Plate 14 shows total BTX loss in groundwater under various treatments. After five weeks of incubation, the enhanced microcosms exhibited a significant reduction (99.8%) in total BTX as compared to the normal or abiotic microcosms. The enhanced microcosms also exhibited a significant reduction (98 percent) in TLH (Plate 15), as compared to the normal or abiotic microcosms.

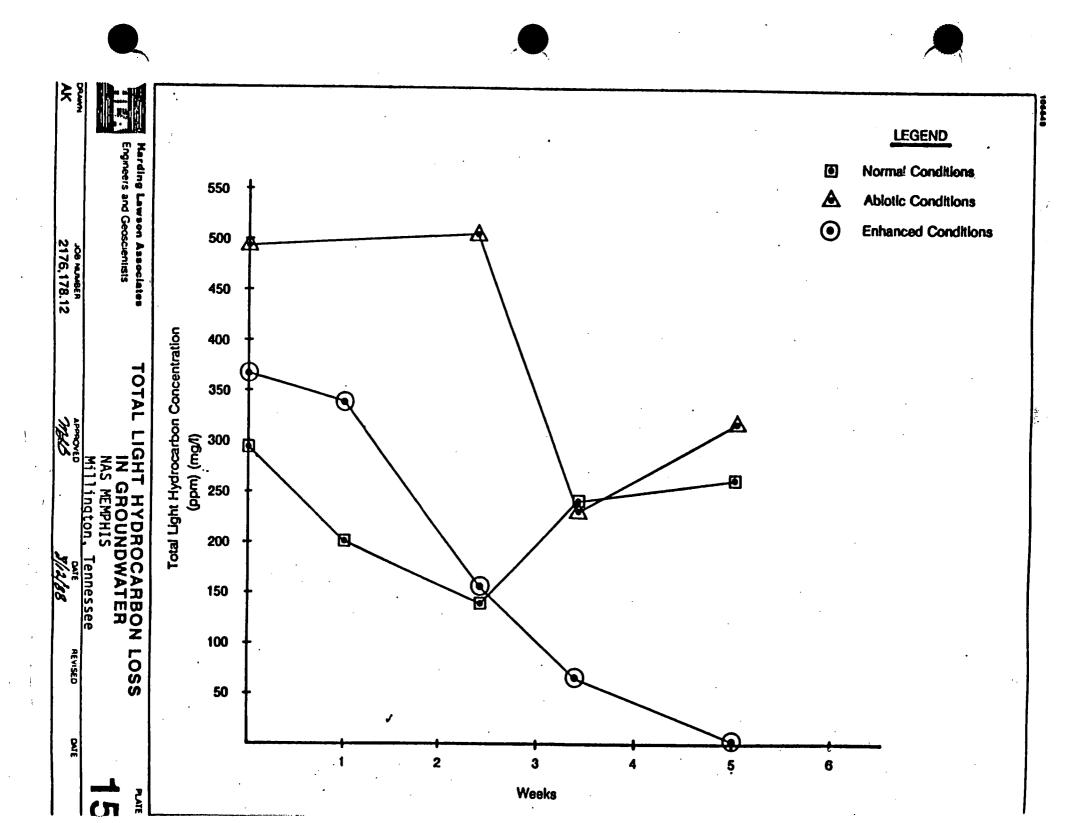
The indigenous microbial populations in the normal and enhanced groundwater microcosms were monitored during the incubation. The disappearance of total BTX and TLH from the soil microcosms under various treatment conditions is depicted in Plates 17 and 18, respectively. The enhanced soil microcosms exhibited a significant decrease in the concentration of total BTX (99%) and TLH (92%); however, the normal and abiotic soil microcosm also exhibited substantial contaminant disappearance. Data points obtained on Week Two of the study were not included in the graphic presentation because all results of chemical analysis performed at that time were abnormal. Possible explanations include the physical heterogeneity of the soil that would affect distribution of the contaminants if the sample were not properly homogenized prior to analyses and laboratory errors involving extraction and/or analysis of the soil samples. Although some variation exists within the collected soil microcosm data, the trend of hydrocarb n disappearance is obvious, and could potentially be increased through the addition of inorganic nutrients and oxygen.

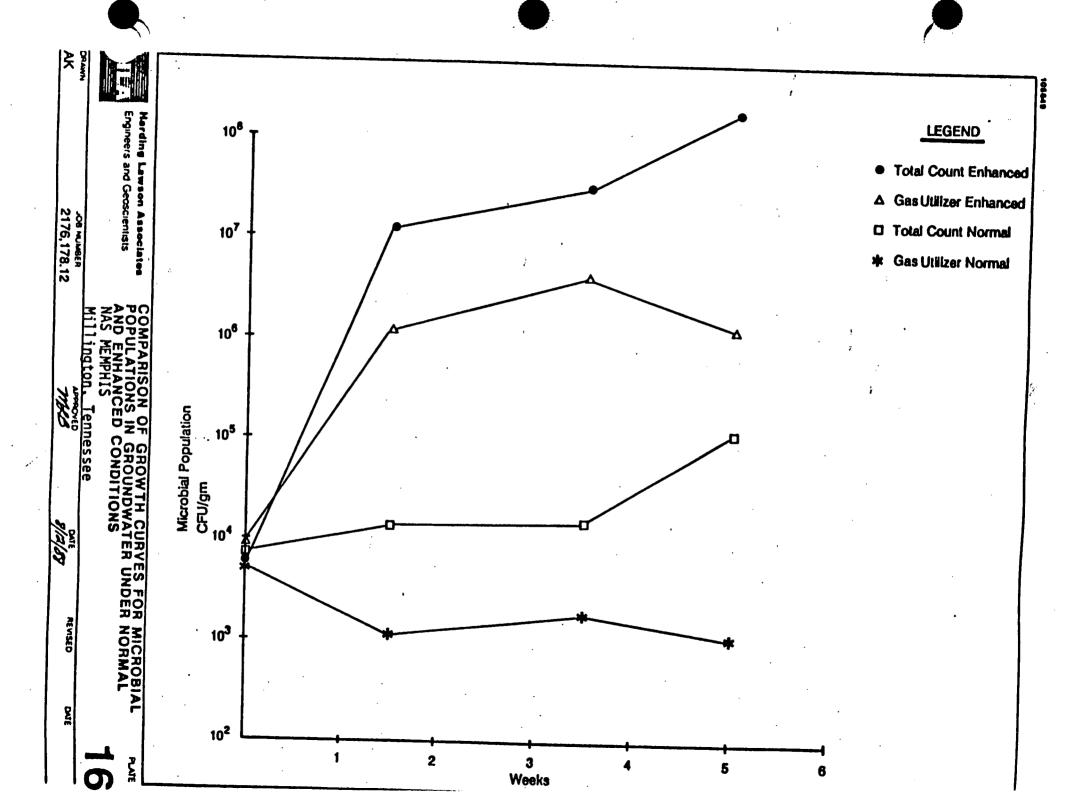
Further support for microbial-mediated hydrocarbon disappearance is presented in Plate 19. Total heterotrophic and gasoline-utilizer microbial populations were monitored in the normal and enhanced soil microcosms during the treatment period. The results show that the total heterotrophic population increased three orders f magnitude in the normal microcosms and four orders of magnitude in the enhanced microcosms. This large increase in the microbial population

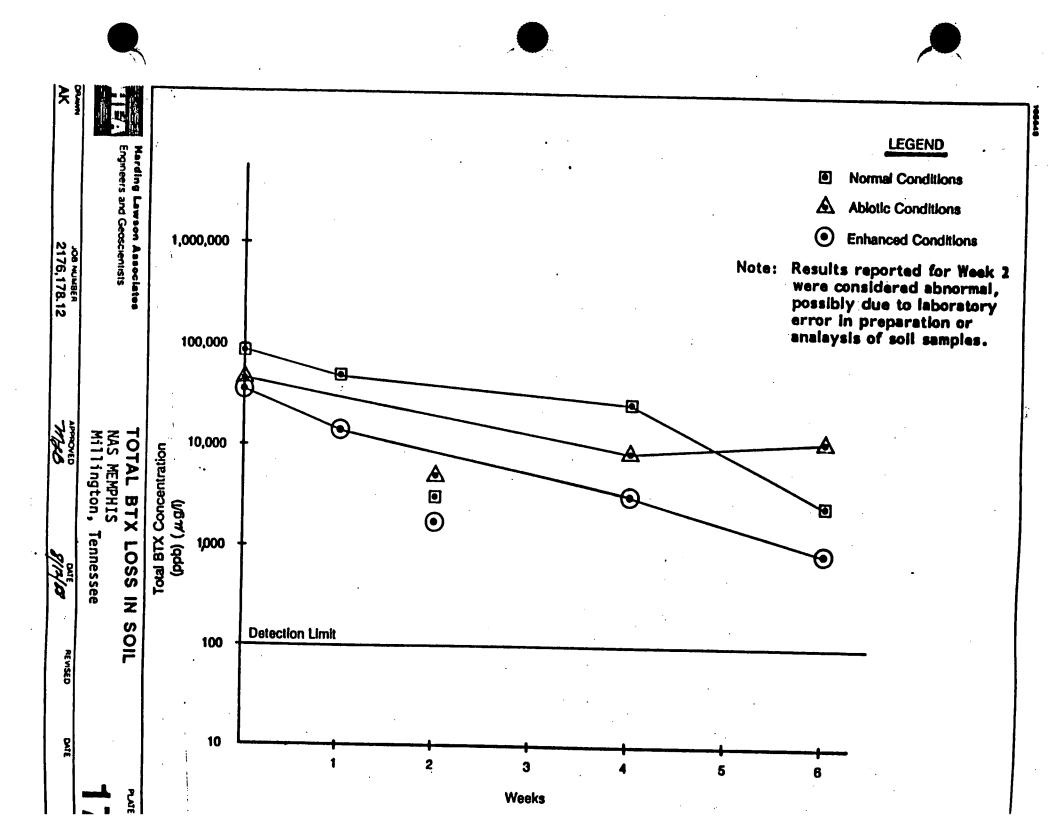
in the normal microcosms could account for the concomitant decrease in hydrocarbon concentration. Additionally, following a lag period of four weeks (microbial processes involving hydrocarbon degradation in soil often exhibit lag periods of several weeks (Reference 7), the gasoline-utilizing microbial population in the enhanced microcosms increased significantly (greater than three orders of magnitude) in the final two weeks of the study. These lag periods are attributed to initial difficulties in obtaining an adequate distribution of nutrients, contaminants, and the necessary microorganisms in a heterogeneous soil matrix.

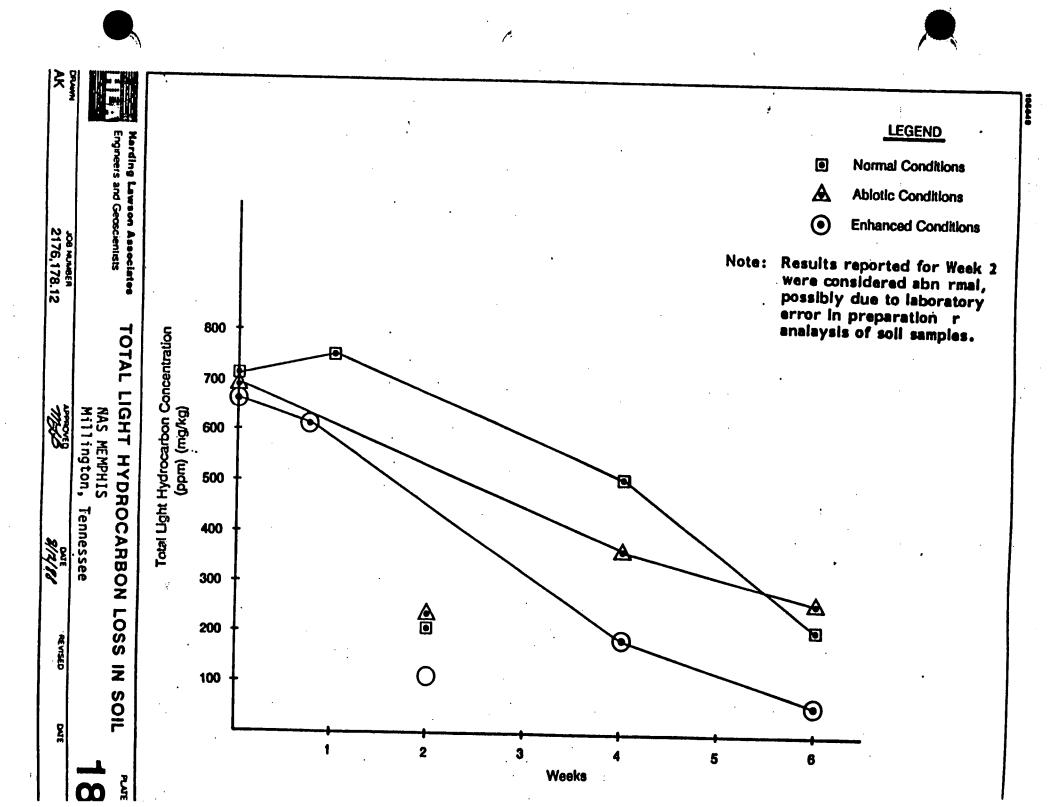
The time constraints associated with the study design did not allow for a complete evaluation of the effect of the observed gasoline-utilizer population increase on the hydrocarbon concentration in the soil over a longer time period.

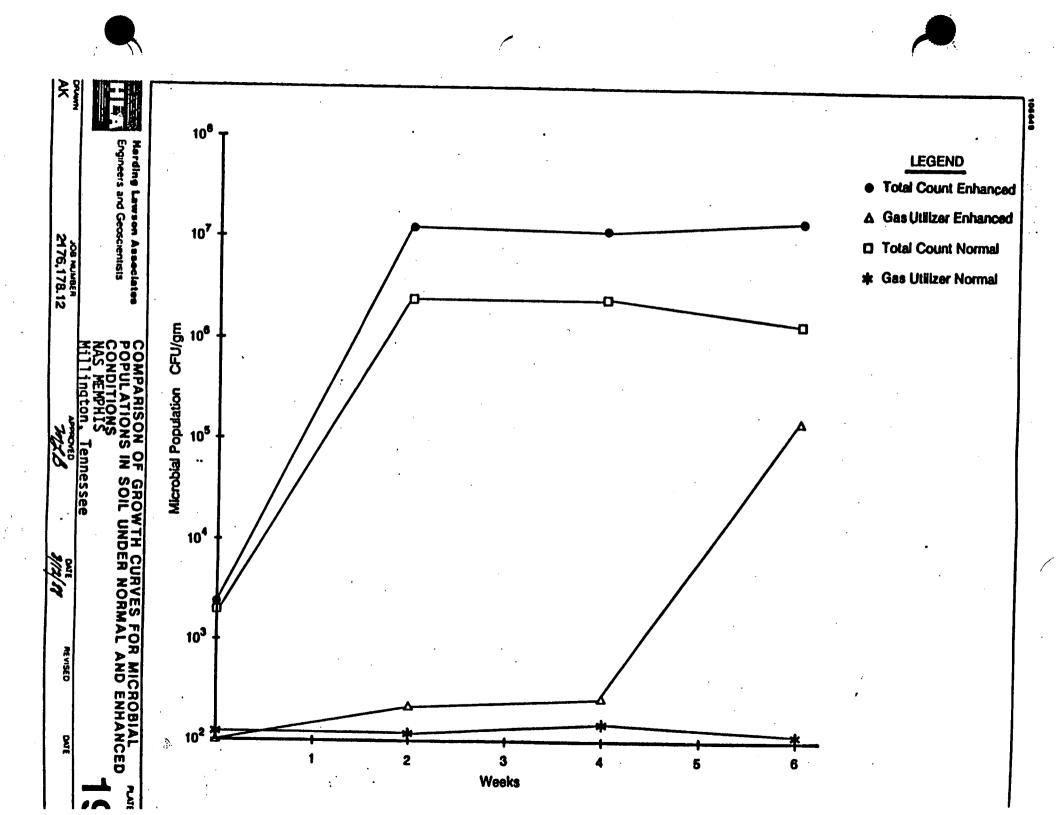












APPENDIX D

LABORATORY DATA SHEETS FOR GROUND WATER SAMPLES TAKEN

DECEMBER 8-12, 1992



Environmental Engineering and Analytical Services

7 F. Greene

orge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

CERTIFICATE OF ANALYSIS

 Laboratory
 Certifications:

 FL
 E87156/87294

 NC
 233

 SC
 10120

 VA
 00151

 TN
 02934

 WI
 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

OA/OC Officer

cc: USGS00191

Project Manager: Pete Ballou

Page N .: 1

Sample ID

: MEM-B1

Lab ID

: 9212325-14

Matrix

: GroundH2O

Date Collected

: 12/09/92

Date Received

: 12/15/92

Priority Collector : Routine : Client

'olatile Organics

BTEX

Benzene

125 ppb

Ethylbenzene

535 ppb

Toluene

165 ppb

Xylenes (TOTAL)

2580 ppb

TPH - Volatile Fraction

35400 ppb



Environmental Engineering and Analytical Services

"ly F. Greene lent

rge C. Greene, P.E., Ph.D. Le President SC Registration No. 9103

CERTIFICATE OF ANALYSIS

 Laboratory
 Certifications:

 FL
 E87156/87294

 NC
 233

 SC
 10120

 VA
 00151

 TN
 02934

 WI
 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

ON/OC Office

cc: USGS00191

Project Manager: Pete Ballou

Page No.:

Sample ID

Lab ID

: 9212325-23

: MEM-B2

Matrix
Date Collected

Collector

: GroundH20 : 12/09/92

Date Received Priority

: 12/15/92 : Routine : Client

Tolatile Organics

BTEX



Environmental Engineering and Analytical Services

v F. Greene

orge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

 Laboratory
 Certifications:

 FL
 E87156/87294

 NC
 233

 SC
 10120

 VA
 00151

 TN
 02934

 WI
 99988775

CERTIFICATE OF ANALYSIS

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

ON/OC Officer

cc: USGS00191

Project Manager: Pete Ballou

Page N .:

Sample ID

Lab ID

: MEM-B3

: 9212325-16

Matrix
Date Collected

: GroundH20 : 12/09/92

Date Received Priority

: 12/15/92 : Routine

Collector

: Client

'olatile Organics

BTEX

Benzene

434 ppb

Ethylbenzene

252 ppb

Toluene

< 20.0 ppb

Xylenes (TOTAL)

487 ppb

TPH - Volatile Fraction

10500 ppb

Comments:

A dilution was required for this sample due to high concentration of target compound(s). As a result, the detection limits are elevated.



Environmental Engineering and Analytical Services

"y F. Greene

orge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

CERTIFICATE OF ANALYSIS

 Laboratory
 Certifications:

 FL
 E87156/87294

 NC
 233

 SC
 10120

 VA
 00151

 TN
 02934

 WI
 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

OA/OC Officer

cc: USGS00191

Project Manager: Pete Ballou

Page N .:

Sample ID

Lab ID

: 9212325-24

: MEM-B4

Matrix

: GroundH20

Date Collected

: 12/09/92

Date Received

: 12/15/92

Priority Collector : Routine : Client

~1166601

7 latile Organics

BTEX

 Benzene
 < 2.00 ppb</td>

 Ethylbenzene
 < 2.00 ppb</td>

 Toluene
 < 2.00 ppb</td>

 Xylenes (TOTAL)
 4.46 ppb

 TPH - Volatile Fraction
 107 ppb



Environmental Engineering and Analytical Services

'ly F. Greene dent

orge C. Greene, P.E., Ph.D. . ice President SC Registration No. 9103

Laboratory Certifications: E87156/87294 NC SC 10120 VA 00151

CERTIFICATE OF ANALYSIS

Date: 12/28/92

TN

WI

233

02934

99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Released by:

Officer

cc: USGS00191

Project Manager: Pete Ballou

Page No .:

Sample ID Lab ID

: MEM-757-1 : 9212325-02

Matrix

: GroundH20

Date Collected

: 12/10/92

Date Received

: 12/15/92

Priority Collector

.: Routine : Client

Volatile Organics

BTEX

Benzene 11000 ppb Ethylbenzene 926 ppb Toluene 5170 ppb Xylenes (TOTAL) 3220 ppb TPH - Volatile Fraction 52000 ppb



Environmental Engineering and Analytical Services

7 F. Greene cni

arge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

Laboratory Certifications: E87156/87294 NC 233 SC 10120 VA 00151 TN 02934 WI 99988779 CERTIFICATE OF ANALYSIS

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/23/92

Released by:

cc: USGS00191

Project Manager: Pete Ballou

Page N .: 1

Sample ID

: MEM-757-2 Lab ID : 9212325-08 Matrix : GroundH20 Date Collected : 12/10/92 Date Received : 12/15/92

Priority Collector : Routine : Client

Volatile Organics

BTEX

3680 ppb Benzene Ethylbenzene 230 ppb 430 ppb Toluene Xylenes (TOTAL) 1160 ppb TPH - Volatile Fraction 23200 ppb



Environmental Engineering and Analytical Services

ont orecas

rge C. Greene, P.E., Ph.D. rice President SC Registration No. 9103 | Laboratory Certifications: FL E87156/87294 | NC 233 | SC 10120 | VA 00151 | TN 02934 | CERTIFICATE OF ANALYSIS | WI 99988779

Released by:

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/23/92

ON/OC OFFICET

cc: USGS00191

Project Manager: Pete Ballou

Page N .: 1

Sample ID

Lab ID

Matrix
Date Collected
Date Received

Priority Collector : 9212325-20 : GroundH2O : 12/10/92

: MEM-757-2R

: 12/10/92 : 12/15/92

: Routine : Client

Volatile Organics

BTEX

Benzene 4600 ppb
Ethylbenzene 302 ppb
Toluene 527 ppb
Xylenes (TOTAL) 1470 ppb
TPH - Volatile Fraction 27500 ppb



Environmental Engineering and Analytical Services

F. Greene ent

Vice President SC Registration No. 9103 RECEIVED USGS-WRD DEC 29 1992

 Laboratory
 Certifications:

 FL
 E87156/87294

 NC
 233

 SC
 10120

 VA
 00151

.

10120 00151 02934

CERTIFICATE OF ANALYSI Columbia, S. C.

TN WI

99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/23/92

ased by:

cc: USGS00191

Project Manager: Pete Ballou

Page N .: 1

Sample ID
Lab ID

: MEM-757-3 : 9212325-01 : Ground#20

Matrix
Date Collected

: 12/10/92 : 12/15/92

Date Received Priority Collector

: Routine : Client

Volatile Organics

BTEX

Benzene	2850 ppb
Ethylbenzene	440 ppb
Toluene	578 ppb
Xylenes (TOTAL)	994 ppb
TPH - Volatile Fraction	12500 ppb



Environmental Engineering and Analytical Services

'ly F. Greene ient

rge C. Greene, P.E., Ph.D. .ce President SC Registration No. 9103

Laboratory Certifications:

E87156/87294 NC 233 SC 10120 VA 00151 02934 TN WI 99988779

CERTIFICATE OF ANALYSIS

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

cc: USGS00191

Project Manager: Pete Ballou

: MEM-757-4

: 9212325-17

: GroundH20

Page No .:

Sample ID

Lab ID

Matrix Date Collected Date Received Priority

: 12/09/92 : 12/15/92 : Routine Collector : Client

'olatile Organics

BTEX

Benzene Ethylbenzene Toluene Xylenes (TOTAL) TPH - Volatile Fraction

< 2.00 ppb < 2.00 ppb < 2.00 ppb < 4.00 ppb < 100 ppb



Environmental Engineering and Analytical Services

Jent Lorge C. Greene, P.E., Ph.D. Vice President

SC Registration No. 9103

CERTIFICATE OF ANALYSIS

Laboratory Certifications: E87156/87294 NC **23**3 SC 10120 VA 00151 02934 TN 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

cc: USGS00191

Project Manager: Pete Ballou

Page No.:

Sample ID

Lab ID

Matrix

Date Collected Date Received Priority

Collector

: MEM-757-4R : 9212325-18

: GroundH2O : 12/09/92 : 12/15/92

: Routine : Client

' latile Organics

BTEX

Benzene Ethylbenzene Toluene Xylenes (TOTAL) TPH - Volatile Fraction

< 2.00 ppb < 2.00 ppb

< 2.00 ppb < 4.00 ppb

< 100 ppb



Environmental Engineering and Analytical Services

y F. Greene ient

urge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

Laboratory Certifications: FL E87156/87294 NC 233 SC 10120 VA 00151 TN 02934 CERTIFICATE OF ANALYSIS 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

cc: USGS00191

Project Manager: Pete Ballou

Page N .:

Sample ID

: MEM-757-5 Lab ID : 9212325-22 Matrix : GroundH20

Date Collected Date Received

: 12/08/92 : 12/15/92 : Routine

Priority Collector

: Client

'olatile Organics

BTEX

Benzene < 2.00 ppb Ethylbenzene < 2.00 ppb Toluene < 2.00 ppb Xylenes (TOTAL) < 4.00 ppb TPH - Volatile Fraction < 100 ppb



Environmental Engineering and Analytical Services

'y F. Greene Laboratory Certifications: **Jent** FL NC 233 rge C. Greene, P.E., Ph.D. SC 10120 ٧A Vice President 00151 SC Registration No. 9103 TN 02934 CERTIFICATE OF ANALYSIS WI 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

ased by: Turk U Name

cc: USGS00191

Project Manager: Pete Ballou

Page No.:

Sample ID
Lab ID

: MEM-757-6 : 9212325-06 : GroundH20

Matrix
Date Collected
Date Received

: 12/09/92 : 12/15/92 : Routine

Priority Collector

: Client

70latile Organics

BTEX

Benzene 165 ppb
Ethylbenzene 27.0 ppb
Toluene < 20.0 ppb
Xylenes (TOTAL) < 40.0 ppb
TPH - Volatile Fraction 603 ppb

Comments:

A dilution was required for this sample due to high concentration of target compound(s). As a result, the detection limits are elevated.



Vice President

Lorge C. Greene, P.E., Ph.D.

SC Registration No. 9103

GENERAL ENGINEERING LABORATORIES

Environmental Engineering and Analytical Services

Laboratory Certifications: E87156/87294 NC 233 SC VA 10120 00151

TN

02934 99988779

CERTIFICATE OF ANALYSIS

Released by:

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

cc: USGS00191

Project Manager: Pete Ballou

Page N .: 1

Sample ID Lab ID

: MEM-757-7 : 9212325-10

Matrix Date Collected : GroundH2O : 12/08/92 : 12/15/92

Date Received Priority Collector

: Routine : Client

'olatile Organics

BTEX

Benzene	115 ppb
Ethylbenzene	265 ppb
Toluene	105 ppb
Xylenes (TOTAL)	2190 ppb
TPH - Volatile Fraction	2680 ppb



Environmental Engineering and Analytical Services

'ly F. Greene dent

Leorge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

FL E87156/87294
NC 233
SC 10120
VA 00151
TN 02934
CERTIFICATE OF ANALYSIS WI 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

Laboratory Certifications:

07/08 055

cc: USGS00191

Project Manager: Pete Ballou

Page No.:

Sample ID
Lab ID

: MEM-757-8 : 9212325-07

Matrix

: GroundH20 : 12/09/92

Date Collected Date Received Priority

: 12/15/92 : Routine

Collector

: Client

70latile Organics

BTEX

Benzene	2050 ppb
Ethylbenz ene	163 ppb
Toluene	613 ppb
Xylenes (TOTAL)	465 ppb
TPH - Volatile Fraction	7530 ppb



Environmental Engineering and Analytical Services

'ly F. Greene dent

Lorge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

CERTIFICATE OF ANALYSIS

Laboratory Certifications: E87156/87294 NC 233 SC 10120 VA 00151 02934 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

cc: USGS00191

Project Manager: Pete Ballou

Page N .:

Sample ID

Lab ID

Matrix

Date Collected

Date Received

Priority Collector : MEM-757-9

: 9212325-19

: GroundH2O

: 12/09/92 : 12/15/92

: Routine : Client

Volatile Organics

BTEX

Benzene Ethylbenzene Toluene

Xylenes (TOTAL)

TPH - Volatile Fraction

< 2.00 ppb

< 2.00 ppb

< 2.00 ppb

< 4.00 ppb < 100 ppb



Environmental Engineering and Analytical Services

y F. Greene

vice President
SC Registration No. 9103

CERTIFICATE OF ANALYSIS

 Laboratory
 Certifications:

 FL
 E87156/87294

 NC
 233

 SC
 10120

 VA
 00151

 TN
 02934

 WI
 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Released by: Tule Billy

QA/QC Officer

cc: USGS00191

Project Manager: Pete Ballou

Page No.: 1

Data: 12/22/92

Sample ID
Lab ID

: MEM-757-10 : 9212325-13 : GroundH20

Matrix
Date Collected
Date Received

: 12/09/92 : 12/15/92 : Routine

Priority Collector

: Client

' latile Organics

BTEX

 Benzene
 < 2.00 ppb</td>

 Ethylbenzene
 < 2.00 ppb</td>

 Toluene
 < 2.00 ppb</td>

 Xylenes (TOTAL)
 < 4.00 ppb</td>

 TPH - Volatile Fraction
 < 100 ppb</td>



Environmental Engineering and Analytical Services

Jent

vice President
SC Registration No. 9103

FL E87156/8729NC 233
SC 10120
VA 00153
TN 02934
CERTIFICATE OF ANALYSIS WI 99988773

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

Laboratory Certifications:

CALCE DELICE

cc: USGS00191

Project Manager: Pete Ballou

Page N .: 1

Sample ID
Lab ID

: MEM-757-11 : 9212325-12

Matrix
Date Collected

Collector

: GroundH20 : 12/08/92

Date Received Priority

: 12/15/92 : Routine : Client

'olatile Organics

BTEX

 Benzene
 5.12 ppb

 Ethylbenzene
 < 2.00 ppb</td>

 Toluene
 < 2.00 ppb</td>

 Xylenes (TOTAL)
 < 4.00 ppb</td>

 TPH - Volatile Fraction
 < 100 ppb</td>



Environmental Engineering and Analytical Services

lly F. Greene ident

orge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

Laboratory Certifications: E87156/87294 NC 233 SÇ 10120 VA 00151 TN 02934 WI 99988779

CERTIFICATE OF ANALYSIS

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/28/92

Released by:

cc: USGS00191

Project Manager: Pete Ballou

Page N .: 1

Sample ID

: MEM-757-12

Lab ID Matrix

: 9212325-05 : GroundH20

Date Collected

: 12/10/92

Date Received

: 12/15/92

Priority

: Routine

Collector

: Client

Volatile Organics

BTEX

Benzene 4240 ppb Ethylbenzene 255 ppb Toluene 603 ppb Xylenes (TOTAL) 696 ppb TPH - Volatile Fraction 10000 ppb



Environmental Engineering and Analytical Services

Jeorge C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

Laboratory Certifications: E87156/87294 NC 233 SC 10120 VA 00151 TN 0293-WI 99988779

CERTIFICATE OF ANALYSIS

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/28/92

cc: USGS00191

Project Manager: Pete Ballou

Released by:

Page No.:

Sample ID

: MEM-757-13 Lab ID : 9212325-04 Matrix : GroundH20 Date Collected : 12/10/92 Date Received : 12/15/92

Priority Collector

: Routine : Client

Volatile Organics

BTEX

Benzene 11700 ppb Ethylbenzene 710 ppb Toluene 3570 ppb Xylenes (TOTAL) 2080 ppb TPH - Volatile Fraction 24100 ppb



Environmental Engineering and Analytical Services

ly F. Greene .dent

George C. Greene, P.E., Ph.D. Vice President SC Registration No. 9103

| Laboratory | Certifications: | FL | E87156/87294 | NC | 233 | SC | 10120 | VA | 00151 | TN | 02934 | CERTIFICATE | OF ANALYSIS | WI | 99988779

Released by:

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

QA/Qe Officer

cc: USGS00191

Project Manager: Pete Ballou

Page N .: :

Date: 12/28/92

Sample ID

: MEM-757-14 : 9212325-03 : GroundH20

Matrix
Date Collected
Date Received
Priority

Collector

: 12/10/92 : 12/15/92 : Routine : Client

Volatile Organics

BTEX

 Benzene
 14000 ppb

 Ethylbenzene
 1130 ppb

 Toluene
 5820 ppb

 Xylenes (TOTAL)
 4020 ppb

 TPH - Volatile Fraction
 24200 ppb



Environmental Engineering and Analytical Services

ly F. Greene dent

orge C. Greene, P.E., Ph.D. vice President SC Registration No. 9103

CERTIFICATE OF ANALYSIS

Laboratory Certifications: FL E87156/87294 NC 233 SC 10120 VA 0015 TN 02934 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

cc: USGS00191

Project Manager: Pete Ballou

Page No .:

Sample ID

Lab ID

: MEM-757-1S €

: 9212325-21

Matrix

: GroundH20

Date Collected

: 12/08/92

Date Received

: 12/15/92

Priority

: Routine

Collector

: Client

70latile Organics

BTEX

Benzene Ethylbenzene Toluene

< 2.00 ppb < 2.00 ppb

< 2.00 ppb

Xylenes (TOTAL)

< 4.00 ppb

TPH - Volatile Fraction

< 100 ppb



Environmental Engineering and Analytical Services

lent George C. Greene, P.E., Ph.D. Vice President

SC Registration No. 9103

CERTIFICATE OF ANALYSIS

Laboratory Certifications: FL E87156/87294 NC 233 SC 10120 VA 00151 TN 02934 WI 99988779

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

cc: USGS00191

Project Manager: Pete Ballou

Page N .:

Sample ID

Lab ID

: MEM-757-16 : 9212325-09

Matrix

: GroundH2O

Date Collected

: 12/08/92

Date Received

: 12/15/92 : Routine

Priority Collector

: Client

7olatile Organics

BTEX

Benzene Ethylbenzene

< 2.00 ppb < 2.00 ppb

Toluene

< 2.00 ppb

Xylenes (TOTAL)

< 4.00 ppb

TPH - Volatile Fraction

< 100 ppb



Environmental Engineering and Analytical Services

F. Greene

orge C. Greene, P.E., Ph.D. vice President SC Registration No. 9103

 Laboratory
 Certifications:

 FL
 E87156/87294

 NC
 233

 SC
 10120

 VA
 00151

Released by

CERTIFICATE OF ANALYSIS

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

02934

99988779

QA/QC Officer

cc: USGS00191

Project Manager: Pete Ballou

Page N .: :

Sample ID

Lab ID

Matrix

Date Collected
Date Received

Priority Collector : MEM-757-17

: 9212325-15 : GroundH20

: 12/08/92 : 12/15/92

: Routine : Client

7olatile Organics

BTEX

Benzene < 2.00 ppb
Ethylbenzene < 2.00 ppb
Toluene < 2.00 ppb
Xylenes (TOTAL) < 4.00 ppb
TPH - Volatile Fraction < 100 ppb



Environmental Engineering and Analytical Services

ient rge C. Greene, P.E., Ph.D. . ice President SC Registration No. 9103

E87156/87294 FL NC SC 10120 VA 00151 TN 02934 99988779 CERTIFICATE OF ANALYSIS W

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

Laboratory Certifications:

/QC Officer

cc: USGS00191

Project Manager: Pete Ballou

Page No.: 1

Sample ID

Collector

Lab ID Matrix

Date Collected Date Received Priority

: MEM-757-18 : 9212325-11 : GroundB20 : 12/09/92

: 12/15/92 : Routine : Client

Volatile Organics

BTEX

Benzene < 2.00 ppb Ethylbenzene < 2.00 ppb Toluene < 2.00 ppb Xylenes (TOTAL) < 4.00 ppb TPH - Volatile Fraction < 100 ppb -



jent

GENERAL ENGINEERING LABORATORIES

Environmental Engineering and Analytical Services

v F. Greene

Laboratory Certifications: E87156/8729-FL NC 23. SC 1012 VA 0015 02934 TN 9998877

rge C. Greene, P.E., Ph.D. ce President SC Registration No. 9103

CERTIFICATE OF ANALYSIS

Client: USGS, Stephensen Center

720 Gracern Road

Columbia, South Carolina 29210

Contact: Dr. Don Vroblesky

Date: 12/22/92

QC Officer

cc: USGS00191

Project Manager: Pete Ballou

Page No.: 1

Sample ID

Lab ID Matrix

Date Collected

: 9212325-25 : GroundH2O : 12/09/92 : 12/15/92

: MEM-757-19

Date Received Priority Collector

: Routine : Client

7olatile Organics

BTEX

Benzene < 2.00 ppb Ethylbenzene < 2.00 ppb < 2.00 ppb Toluene Xvlenes (TOTAL) < 4.00 ppb TPH - Volatile Fraction < 100 ppb

CHAIN OF CUSIODY RECORD

General Engine ratories 2040 Savage Roso Charleston, South Carolina 29414 PO Box 30712 Charleston, South Carolina 29417

Page 2 of 2 Client Name / Facility Name 803-556-8171 SAMPLE ANALYSIS REQUIRED(x) - use remarks area to specify specific compounds or methods Use F or P in the boxes to indicate whether U.S. Geologica Survey
Collected By Company
Frank Chapelle 4. sample was filtered and/or preserved TOC / DOC ХŌТ TIME SAMPLE ID Remarks BTEX + TPH MEM -B1 12-9-52 MEM 757-17 12-8-94 MEM-03 12-9-92 MEM-757-4 12-9-92 11 MEM 757 -4R 12-9-92 11 MEM 757 -9 12-9-92 11 11 MEM 757-21 12-10-92 MFM757-15 12-8-92 11 11 MEM 757-5 12-8-92 10 MEM-B2 12-9-92 MEA - BY 129-92 11 MEM 757-19 12-9-92 11 Received by: Reliequished by: Date Received by: 12-15-48 1325 Remarks

12-15-12/505

White • sample collector Yellow • file Pink • with report



General Enginer oratories
2040 Savage Road
Charleston, South Carolina 29414
PO Box 30712
Charleston, South Carolina 29417
R03-556-8171

Page 1 of 2					·										•												C	Charle	ox 30712 eston, Sci <u>56-</u> 8171	outh Caroli	ina 294	417
Client Name / Facility Name	• /	70	-		T	T	<u>s/</u>	AMPL	EAN	NALYSI	S RF	EQUIP	(ED(x)	· USF	e rema	rks ar	rea lo	speci	ify sp	ecific	compr	ounds	or m	ethods		Use F				rdicate whell	they	
U.S. Geolo	DAICH	ノンい	rı	UZ.	\ \	2	Ц	口'	Д.	丑	口	丁	耳	П	卭	Ť	Д		二"		Ш	П	Ĭ	Ф	다				and or pr		/er	
Collected By / Company	')'		/	<u> </u>		S		1		ब			3						[, '	1	1	2					_	-				
Frank	40	-00	7		´ l '	contain	1	10	1	, g	g	آچٍ ا	4 8	.			_ '	ig	bld.	1	1	pecify										
Trank	- may	eru	'				1	8 8	1	Ę	15	1 2 5	وَ عَ	۔ ا	و ا ـ	, ?	8	, g .	1 2 '	1	1	1.		l								
SAMPLE ID	DATE	TIME	널	[일				1 ~ 1	×	8.9	Nitrite/Nitra	VOC - Spec	Method ra	Perticide	Herbicide	, E	Total Pheno	Acid Extra	B/N Eura	15		Coliforn			-							
SAMIFLE ID	DAIL ,	LIIVIL		N P P P P	鼠.	*1"	弘	ဥ	ě	Chloride, Fluoride, Suffate	人艺	27	2 2	1	里	في إ	4	Ş.	8	ĝ	Cyanid	3	<u> </u>	L	Ŀ			7	Remar	.rks		
	,		\mathbf{J}	$\prod I$		7		()		T		1	1		1	T	T						T	1	7		7+				n //	
MEM 757-3	12-10-52	4.]]	$i \mid I$				1 '	1	'		17	V		1		ŀ	: J	1 '	1 '		1				r	517	<i>上</i> >	X of	-TI	PH	
	 	 	#	4	4	十	7	$\overline{}$		1	1	*	*	:	+	+	+	,—+	_	+	+	+-	+	+	+		<u>/., -</u>	<u></u>				
MEM 757-1	12-10-97	<u>.1</u>		1 1			J	1 '	1 .	. [·	1	ТУ	A:	-)	i '	1	1	1		ļ					70			
111111111111111111111111111111111111111			++	H	+	+	-	_	1	'	+-	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	4-	+-	+	+	+		<u></u> '	+-'	+	+-	+	-	—					<u> </u>		
MARA TO TH	اره در ما		$\cdot 1$	$I \mid I$			1	1 '	1 3	4		1	/];			1	.]	1 '	1 '	.	l	'	Ì					l(.			
MEA 757-14	12-10-70	12:	Ш	\Box	4	—		<u>'—</u> ــــــــــــــــــــــــــــــــــــ	_	┷,				Ŀ			_		<u> </u>	'ـــــــــــــــــــــــــــــــــــــ	<u> </u>		\perp	\bot	\perp			1	· /)			
k n	1'	1	11	$I \cup I$		- 1		1 1	1	'		1	/				1.	. 1	ί '		[· '		T	Ţ	7			1				
MEM 757-13	12-10-12	4			1 k			1 1	1	'	1		J					J	ι '	1 '	1	;		ı				•				
••			T	T	T	1		6.				1	T		. 🕇	+	1		1	1	_	1	+	+	+				•			
MEN 757-12	412-1092	1		$I \mid I$		1		$C^{\prime\prime}$	1	'	1:	ΙX	J.	1			-	.]	1 '	1 '	1 '	1		İ	1			:	((
	1	 	++	4	+	+	+	<u>, </u>		+	+	41	4	+-	+-	+	+	-		1	1-	+	+		+							
MAKIN 757-6	11 -9-97			1 1			1	1 1	1. '	'		ΙX	4				- '	.]	1. 7	1 '	1 '	1.					•		1(
MEM 757-6	112 1 15	1	44	4	+	+		لسب	4-	 '	4:	八	4	4		4	+	<u>.</u>	''	4'	4_'	4_	4	_					1			
1	112-9-9-	1	\mathbf{I}	$\iota \mid \mathcal{F}$	11			1 1	1 . '	1 '	1.	1\/	∕1. ∗		·				1 1	1. '	1 '	1	1						1/		_	_
MEM 757-8	14-1-10	<u>†</u>	Ш	4	4	1			<u>'</u>	'		A		L.		L	1]	1_1	1_'	'			L					ll .	·	'	
	1	r	T	171	Π			i^{-1}	(·	T. '			1	,	1	T	T	7						T	T				,,	-		
MEM 757-2	12-10-57	4		71				₁ 1	1 '	1. '	1	IX						- }	_i , j	1 '	1 '	1	1.						11			
			11	1	一	+	7	\leftarrow	_	1-	—	1	;	1	+	+	+	+		-	_	1	+	+	+			-	`			
MEM757-16	12-8-57	A		$\iota \mid J$			1	₍)	1 : '	1 ' '	1	X	.1		1				, J	1 '	1	1			1				ıl			
, , , , , , , , , , , ,	1,200	1	++	4	+	+	+	Щ,	 '	+-	+-	+:-	 	+	+	4-	+	+++	لــــ	1-	 '	+	+	+-	+				('			
MEM 757 - 7	1: 40	1		(\Box)		1	,	1 1	1	1 '	1	Ιγ	47		1			:	,)	1 '	1 '	1	1					•	11			
MEMILI	12-8-76	 '	4	4	4	4		النب	— '	 '	4_ '	17		1			4			<u>'</u>	 '								υ,			
1.	1'		11					, J	4'	1 .'	.1	$\mathbf{J}_{\mathbf{\lambda}}$	<i>}</i> '	1		1.	- 1		, 1	1 7	1 '	1				•				 ,	-	
MEM 757-18	12-7-70	1		Ш	山				('	<u>'</u>		IX	. ['				L		, _)	1_1	1_'	1_'		· [_					11		_	
1 '	1	1.	П	TI	T	T		1.		一 ,		V	1.		1		T				1			1	1							
MEM 757-11 MEM 757-10	112-8-92	4	11	4 1	<i>i</i>]			<i>i</i> 1	1 '	1.7	1	X	, l '	1.	.				,)	C^{1}	1 '	1		1.	-			,	11			
	1 - 1		+	4	十	+			<u></u>	 	1-	1	+	+	+	+	+	1			_	1-	+	+	+				`			*
MEM 757-10	112-5-92	4 '	1.1	4 1	<i>i</i> [, ,	1 '	1 1	1.	17	<i>i</i>	1			'		,)	1 1	1 '	1	1.	11				(1			
Delineriched We / //	Carrier and the second second		Time	خلك	1 R/	eceived		لــــــــــــــــــــــــــــــــــــــ		ســــــــــــــــــــــــــــــــــــــ	<u>`</u>	س	'ہــــــــــــــــــــــــــــــــــــ		llequishe	4				لسنسا	لسا	4	Date	جلد	Time		Denel	ived by:		AND CHEMICAL		حبج
Bolinquished by		12-159			<i>ተ</i> ~	A	ν,	.:		4				Ku.	. Admir.	AL UZ.	•					- 1	Jen. I	٠,	1,100-	′ 1	Misse	/80 vy.	· ·			
Relinquished by			Time		TRO!	(el)	4 by 1	lah by		A	1		1	Date		Time	9	77	Remark	ats.		L			4							
,		4 4	4	•.,	1 7	TV	i /a	4 4	· iK	/ (n.	.lr	. 0	1 1	-		190		, ,	•	_												

White • sample collector

Yellow • file Pink • with rennet